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Carbon nanotubes enhanced Seebeck coefficient and power factor of rutile TiO₂

Yao-Cheng Lai, Hsin-Jung Tsai, Chia-I Hung, Hiroyuki Fujishiro, Tomoyuki Naito, and Wen-Kuang Hsu

Seebeck coefficient, according to Ioffe’s approximation, is inversely proportional to carrier density and decreases with doping. Here we find that incorporation of multi-walled carbon nanotubes into rutile TiO₂ improves electrical conductivity and Seebeck coefficient at low filling fraction of tubes; the former is owing to lengthening of mean free path and doping modified carrier mobility for the latter. Tube-oxide mixing also causes significant phonon drag at interfaces and reduced thermal conductivity is verified by promoted figure of merit.

Introduction

Materials that show potential in thermoelectric powering (TEP) have drawn much attention in recent years. Three factors determine efficiency of energy conversion at a given temperature (T) and can be linked through a dimensionless parameter known as figure of merit ZT = TσS²/k, where σ is electrical conductivity, S is Seebeck coefficient, σS² is power factor and k is thermal conductivity. Scattering plays a crucial role in determining σS² and has been verified by alloying Bi with Sb and Te. Study reveals that alloying creates multi-domains and carriers encounter a Schottky-like barrier at interfaces. In this case, interfacial scattering occurs and reduced k leads to ZT promotion. Cited alloys however are toxic in nature and produce environmental issue. Accordingly, seeking of replacements becomes important and study currently focuses on oxides, including ZnO, CaMnO₂, NaCo₂O₄, Ca₃Co₄O₁₁, In₂O₃SnO₂ and TiO₂.

Oxides, however, lack of free carriers and large σS² only emerges at high T, e.g. In₁₋ₓSnₓO₂ gives σS² = 1.6×10⁴ Wm⁻¹K⁻¹ at T = 1300 K. Doping may promote carrier density (n) to some extent and has been carried out on CaMnO₃ using Bi as dopants. ZT however does not significantly increase with doping and underlying mechanism has been interpreted according to the Ioffe’s approximation:

$$S = \pm \frac{k_B}{e} \left[ r + 2 + \frac{2(2\pi n m^* k_B T)\frac{3}{2}}{h^3 n} \right]$$

where k_B is Boltzmann constant, e electron charge, r is absolute scattering factor, m* is effective mass and h denotes Planck’s constant. Equation clearly indicates that S is inversely proportional to n (i.e. S ∝ n⁻¹) and σ is improved at the expense of S. TiO₂ is eco-friendly and its photo-catalytic character has been proved capable of promoting charge storage in solar cell as well as supercapacitor. He et al have studied the TiO₂ at T = 20°C and found a positive S at x = 1.2-1.7. S then transits into negative at x = 1.7 and reaches the maximum at x = 2. TiO₂ shows a low σS² and ZT lies on 0.1-0.2 at T = 700-1100 K. In this work, multi-walled carbon nanotubes (MWCNTs) are thermally mixed with rutile TiO₂ and resultant composites exhibit increased σ and reduced k at a low filling fraction of tube (fCNT), i.e. amplified σ/k. Both k and σ significantly increase as fCNT approximates electrical percolation threshold (τ) and improvement is owing to tube networking. Surprisingly, S is also promoted and displays S ∝ fCNT prior to τ. S then decreases and approaches the positive regime at fCNT ≈ τ, indicative of p-type CNTs governed TEP. Study here shows TEP improvement by 5553% for σS² and 7380 % for ZT at T = 300-523K.

Experimental

Synthesis

MWCNTs (95% purity, Legend Star International Co., Ltd) and TiO₂ (P25, average particle size ~25nm, Aldrich) are dispersed in ethanol using a planet ball milling (290 rpm, ball size = 3 mm and 4 h). Dispersion is then dried at 60°C and remaining solid mixture is sintered by spark plasma sintering (SPS) technique at 1200 K; the CNT content in oxide being 0.1 wt% (TC₀.1), 0.5 wt% (TC₀.5), 1 wt% (TC₁), and 10 wt% (TC₁₀) respectively.

Materials Characterization

Composite texture is inspected by scan electron microscopy (SEM) and the bonding characters are analysed using raman and X-ray photoelectron spectroscopy (XPS). A four-wire technique is employed to probe σ and S at 300-523 K; the former is carried out using a Keithley-4200 power supply with background noise controlled at ± 0.5 nA. The k is determined according to equation k = ϕCₚρ, where ρ is material density, Cₚ is heat capacity and ϕ is thermal diffusivity. First, samples are pressed into pellets and are sandwiched between thin carbon
films as reference. Second, $\varphi$ and $C_p$ are probed by the laser-flash technique (LFA-447) and differential scanning calorimetry (DSC) at 10°C/min.

Sintering causes fusion and oxide particles become interconnected (Fig. 1(a)). Addition of CNTs into oxide creates low resistance paths and joule heating takes place mainly at embedded tubes. Accordingly, oxides remain granulated and are decorated with dispersed tubes (Fig. 1(b)).

Band structure, including energy gap ($E_g$) and LUMO/HOMO states at $E_F$, is calculated using ab-initio method (CASTEP) as follows. First, an extended oxide structure is built in a $2\times2\times2$ superlattice and is geometrically optimized with the generalized gradient approximation (GGA). Second, the ultrasoft pseudopotential and Monkhost-Pack grid are set at 480 eV and 0.05Å$^{-1}$. Third, the $m^*$ at the minimum of LUMO and maximum of HOMO is determined according to equation below.

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}$$

where $\hbar$ and $k$ are reduced planck constant and wave-vector and, the $E(k)$ denotes energy with respect to $k$. Similar procedures are also applied to carbon doped oxide structure with doping content of 0.1wt%. For the sake of accuracy, $E_g$ is also measured by diffuse-reflectance uv-vis spectroscopy and obtained data is fit with equation $\alpha h\nu = C(\hbar\nu - E_g)^\gamma$ where $\alpha$ is linear absorption coefficient, $\nu$ is incident frequency, $C$ is proportionality constant and $\gamma$ is a constant determined by $E_g$, i.e. $\gamma = 0.5$ for direct $E_g$ and $\gamma = 2$ for indirect $E_g$.

Results and discussion

Fig. 1. SEM images of pure oxide (a) and TC$_{0.1}$ (b) and corresponding Raman spectra (c).

Fig. 2. XPS spectra of TC$_1$ at 280-294 eV (a) in comparison with oxide at 454-468 eV (b).
Fig. 3. The ab-initio simulated structure of pure oxide (a) and carbon doped oxide (b) and corresponding Mulliken charge dispersion of oxide (c) and doped oxide (d).

Fig. 4(a) displays $\sigma$ profiles of pure oxide (red), TC$_{0.1}$ (blue), TC$_{0.5}$ (green), TC$_1$ (pink) and TC$_{10}$ (yellow) at 300-523K. We find that improvement reaches one order of magnitude for TC$_{0.1}$, TC$_{0.5}$ and TC$_1$ and $\sigma \propto T$ is attributable to Boltzmann energy ($k_B T$) created carriers in CNTs$^{21}$. For TC$_{10}$, $\sigma$ increases by two orders of magnitude relative to oxide alone, confirming $\tau \sim f_{\text{CNT}} = 10$ wt%.

Two factors contribute to $\sigma$ enhancement according to equation $\sigma = n e^2 \eta / m^*$ where $\eta$ is mean free path controlled relaxation time. Apparently, the $\eta$ prevails and $n$ increase due to carbon doping is limited. First, pure oxide has an $E_g$ of 3.03 eV at $\Gamma$ point and doping created n-type state lies at 2.674 eV (Fig. 4(b)). At 300K, the $k_B T$ (= 0.0259 eV) is too low to create thermal carriers through band-to-band transitions, including valence band$\rightarrow$doped state ($\Delta E_{v-d}$ = 2.674 eV), doped state$\rightarrow$ conduction band ($\Delta E_{d-c}$ = 0.356 eV) and valence band$\rightarrow$ conduction band ($\Delta E_{v-c}$ = 3.03 eV) (Fig. 4(b)). Second, the sequence of $k_B T < \Delta E_{d-c} < \Delta E_{v-d} < \Delta E_{v-c}$ remains at 523K ($k_B T_{523K} = 0.045$ eV), indicative of unchanged $n$. Third, the uv-vis spectra support calculation and $E_g$ is found to be 2.89 eV for oxide, 2.48 eV for TC$_{0.1}$, 2.41 eV for TC$_{0.5}$, 2.28 eV for TC$_1$ and 1.67 eV for TC$_{10}$, exceeding $k_B T$ at 300K and 523K (Table 1 & Fig. 5(a)).

Fourth, $S$ is promoted from 470 $\mu$VK$^{-1}$ (oxide) to 550 $\mu$VK$^{-1}$ (TC$_{0.1}$) at 300K and from 500 $\mu$VK$^{-1}$ to 610 $\mu$VK$^{-1}$ at 523K, in contradiction with $S \propto n^{-1}$ (Fig. 5(b)). $S$ then significantly decreases and approaches the positive regime at TC$_{10}$, again supporting p-type CNTs governed TEP (yellow, Fig. 5(b)).

Table 1. $E_g$ at various $f_{\text{CNT}}$ in comparison with pure oxide.

<table>
<thead>
<tr>
<th>Samples</th>
<th>oxide</th>
<th>TC$_{0.1}$</th>
<th>TC$_{0.5}$</th>
<th>TC$_1$</th>
<th>TC$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$ (eV)</td>
<td>2.89</td>
<td>2.48</td>
<td>2.41</td>
<td>2.28</td>
<td>1.67</td>
</tr>
</tbody>
</table>

CNTs conduct heat and are often dispersed in polymers to improve $k$. Incorporation of CNTs into a polymer, however, induces heat resistance at interfaces and effective thermal conduction appears to rely on tube-polymer cohesion$^{13}$. The oxide-tube coupling, according to SEM inspections (Fig. 1(a)-(b)), is weak and enhanced scattering at interfaces is expected$^{13}$. Measurements carried out at 300K yield $k = 3.05$ Wm$^{-1}$K$^{-1}$ for oxide and 2.2-2.39 Wm$^{-1}$K$^{-1}$ for TC$_{0.1-1}$, supporting enhanced scattering at tube/oxide contacts (Fig. 6(a)). Conduction paths are then switched from bulk oxide to tubes at $f_{\text{CNT}} \sim \tau$ and conversion is supported by (i) significant $k$ increase and (ii) Umklapp process induced $k \propto T^{-1}$ in CNTs$^{22}$; the latter being measured to be 3.02 Wm$^{-1}$K$^{-1}$ at 300K and 2.4 Wm$^{-1}$K$^{-1}$ at 523K.
Fig. 5. The uv-vis spectra (a) and S profiles (b) of oxide and composites.

Fig. 6(b) plots $\sigma S^2$ against $f_{CNT}$ at 300-523K. Again, improvement is evident by a large gap between pure oxide and TC$_{0.1}$; the former lies on $10^{-7}$ Wm$^{-1}$K$^{-2}$ and $10^{-5}$ Wm$^{-1}$K$^{-2}$ for the latter. ZT profiles display a similar trend and gap also reaches two orders of magnitude (Fig. 6(c)). It is worth mentioning that ZT improvements here may not be as large as reported data whereas simultaneous increase in $\sigma/k$ and $S$ is novel and has not been previously observed. Table 2 compares TC$_{0.1}$ with recent reports on single-walled CNTs (SWCNTs)- and graphene-based composites: the negative sign and numbers in brackets indicate negative enhancement and increase with respect to initials. First, addition of CNTs and/or graphenes into TEP matrix results in reduced $k$, supporting enhanced scattering at interfaces. Second, ZT in MWCNTs/ WS$_2$ and graphene/PbTe systems is promoted at the expense of $S$. Third, SWCNTs/Bi$_2$Te$_3$ shows improved $S$ and reduced $\sigma$, thus giving a finite ZT enhancement. Fourth, TC$_{0.1}$ here shows increased $\sigma/k$ and $S$ and, ZT is enhanced by 7380%. Questions however remain as to why $S$ increases at low $f_{CNT}$. According to the Ioffe’s approximation, $S$ also varies with $m^*$ and is therefore expected to change upon doping. Table 3 lists $m_e^*/m_o$ and $m_h^*/m_o$ along crystallographic planes of [100], [010] and [001] where $m_e$, $m_h$ and $m_o$ are masses of electron, hole carriers and free electrons. Note that the $m_h^*/m_o$ along [001] plane may be ignored because $\sigma$ is mainly contributed by carriers that have a lower $m^*$ and move along electric field. Calculation shows increase by 61% ($m_e^*/m_o$) and 27% ($m_h^*/m_o$) along [100] plane, supporting doping modified carrier mobility. The $m_e^*/m_o > m_h^*/m_o$ also takes place at [010] plane and increase is measured to be 62% and 25%.

Table 2. TEP parameters of TC$_{0.1}$ in comparison with reported data at room T

<table>
<thead>
<tr>
<th>TEP Samples</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$S$ (µVK$^{-1}$)</th>
<th>$\sigma S^2$ (µWm$^{-1}$K$^{-2}$)</th>
<th>$k$ (Wm$^{-1}$K$^{-1}$)</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT$_{0.5,15%}$</td>
<td>200 (50%)</td>
<td>231.2 (65.1%)</td>
<td>1069 (36.4%)</td>
<td>1.20 (-13%)</td>
<td>0.27</td>
</tr>
<tr>
<td>/Bi$_2$Te$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWCNT$_{0.5,15%}$</td>
<td>3 (12300%)</td>
<td>510 (-22%)</td>
<td>68.4 (7330%)</td>
<td>3.3 (-43.1%)</td>
<td>6.21x10$^{-7}$</td>
</tr>
<tr>
<td>/WS$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(12783%)</td>
</tr>
<tr>
<td>Graphene$_{3,5%}$</td>
<td>234 (1021%)</td>
<td>200 (-46.67%)</td>
<td>936 (289%)</td>
<td>0.93 (-51.8%)</td>
<td>0.3</td>
</tr>
<tr>
<td>/PbTe$^{25}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(602%)</td>
</tr>
<tr>
<td>Graphene$_{2,5%}$</td>
<td>30 (10.42%)</td>
<td>240 (-5.88%)</td>
<td>173 (-2.26%)</td>
<td>3.825 (-1.29%)</td>
<td>1.36x10$^{-4}$</td>
</tr>
<tr>
<td>/CuInTe$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(-1.02%)</td>
</tr>
<tr>
<td>TC$_{0.1}$</td>
<td>0.71 (4249%)</td>
<td>552.8 (14%)</td>
<td>21.5 (5553%)</td>
<td>2.43 (-24.8%)</td>
<td>3.04x10$^{-7}$</td>
</tr>
</tbody>
</table>

The numbers in brackets denote increase % with respect to initials and negative sign indicates a negative enhancement.
Conclusions
CNTs/TiO$_2$ composites made by SPS technique exhibit increased $\sigma/k$ and S and the underlying mechanism involves lengthening of mean free path and $m^*$ change upon tube addition. The weak tube-oxide coupling induces interfacial scattering and results in reduced k. S is negative at low f$_{\text{CNT}}$ and increases from TC$_{0.1}$ to TC$_{1}$. TC$_{10}$ is governed by p-type CNTs and S decreases toward positive regime. Tube addition creates doped state below LUMO and $m^*/m_o$ increases by 61-62% along (100) and (010) planes, accounting for increased S.

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Notes and references
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References


