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*∗

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

Introduction

Materials that show potential in thermoelectric powering (TEP) have drawn a lot of attention in recent years. Three factors determine the efficiency of energy conversion at a given temperature (T) and can be linked through a dimensionless parameter known as the figure of merit $ZT = \sigma S^2 T/k$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $\sigma^2$ is the power factor and $k$ is the thermal conductivity.1 Scattering plays a crucial role in determining $\sigma^2$ and has been verified by alloying Bi with Sb and Te.2,3 Studies reveal that alloying creates multi-domains and carriers encounter a Schottky-like barrier at the interfaces.4 In this case, interfacial scattering occurs and reduced $k$ leads to a ZT promotion.5 However, the cited alloys are toxic in nature and produce environmental issue. Accordingly, the search for replacements becomes important and studies currently focus on oxides, including ZnO, CaMnO3, NaCo2O4, Ca3Co4O9, In2O3, Cu2O, SnO2 and TiO2.4–7

Oxides, however, lack free carriers and large $\sigma^2$ values only emerge at high $T$, e.g. In2O3·SnO2 gives $\sigma^2 = 1.6 \times 10^{-6}$ W m$^{-1}$ K$^{-2}$ at $T = 1300$ K.4 Doping may promote the carrier density ($n$) to some extent and has been carried out on CaMnO3 using Bi as the dopant.5–7 However, the ZT does not significantly increase with doping and the underlying mechanism has been interpreted according to Ioffe’s approximation:

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

where $k_B$ is the Boltzmann constant, $e$ is the electron charge, $r$ is the absolute scattering factor, $m^*$ is the effective mass and $\hbar$ denotes Planck’s constant.8 The equation clearly indicates that $S$ is inversely proportional to $n$ (i.e. $S \propto n^{-1}$) and $\sigma$ 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 cells as well as supercapacitors.9 He et al. have studied TiO2 at $T = 20$ °C and a positive $S$ value was found at $x = 1.2–1.7$. S then transits into a negative value at $x = 1.7$ and reaches the maximum at $x = 2$.10 Again, TiO2 shows a low $\sigma^2$ value and the ZT lies on 0.1–0.2 at $T = 700–1100$ K.10,11 In this study, multi-walled carbon nanotubes (MWCNTs) are thermally mixed with rutile TiO2 and the resultant composites exhibit increased $\sigma$ and reduced $k$ at a low filling fraction of tubes ($f_{CNT}$), i.e. amplified $\sigma/k$. Both $k$ and $\sigma$ significantly increase as $f_{CNT}$ approximates the electrical percolation threshold ($\tau$) and the improvement is because of tube networking. Surprisingly, $S$ is also promoted and displays $S \propto f_{CNT}$ prior to $\tau$. $S$ then decreases and approaches the positive regime at $f_{CNT} \sim \tau$, indicative of p-type CNTs governed TEP. The study here shows TEP improvement by 5533% for $\sigma S^2$ and 7380% for ZT at $T = 300–523$ K.

Experimental

Synthesis

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

Materials characterization

The composite texture was inspected by scanning electron microscopy (SEM) and the bonding character were analysed.
using Raman and X-ray photoelectron spectroscopy (XPS). A four-wire technique was employed to probe $\sigma$ and $S$ at 300–523 K; the former was carried out using a Keithley-4200 power supply with the background noise controlled at ±0.5 nA. The $k$ was determined according to the equation $k = \varphi C_p \rho$, where $\rho$ is the material density, $C_p$ is the heat capacity and $\varphi$ is the thermal diffusivity. First, the samples were pressed into pellets and sandwiched between thin carbon films as a reference. Second, $\varphi$ and $C_p$ were probed using the laser-flash technique (LFA-447) and differential scanning calorimetry (DSC) at 10 °C min$^{-1}$.

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

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

where $\hbar$ and $k$ are the reduced planck constant and wave-vector, respectively and $E(k)$ denotes the energy with respect to $k^2$.

Results and discussion

Sintering causes fusion and oxide particles to become interconnected (Fig. 1(a)). The addition of CNTs into the oxide creates low resistance paths and joule heating takes place mainly at the embedded tubes. Accordingly, the oxides remain granulated and are decorated with dispersed tubes (Fig. 1(b)). Fig. 1(c) displays the Raman spectra of sintered oxide (red) in comparison with TC$_{0.1}$ (green). For the rutile phase, the Raman-active modes due to site symmetry appear at 143 cm$^{-1}$ ($B_{1g}$), 447 cm$^{-1}$ ($E_g$) and 612 cm$^{-1}$ ($A_{1g}$), along with a broad feature arising from multi-phonon processes at 235 cm$^{-1}$ (red).$^{16-18}$ The $E_g$ mode gets shifted ($\approx$ 9 cm$^{-1}$, green) as tubes are added and the phenomenon may come from carbon doping. First, the XPS spectra exhibit C1s peak at 284.6 eV and distinguishable features at 286.4 eV and 288.5 eV, which corresponds to C–O and C–O bonds (Fig. 2(a)).$^{19}$ Second, the $E_g$ mode was nonpolar in nature and the mode frequency was essentially determined by the bond length and strength.$^{17}$ In other words, Ti was replaced by C and carboxyl forms. Third, carbide (TiC) was absent in the XPS spectra, excluding O–C substitution. Fourth, doping induces a blue-shift in the Ti$^{4+}$ spectra and the peaks move by 0.25 eV for Ti$\!2p_{3/2}$ (463.7 eV) and 0.3 eV for Ti$\!2p_{1/2}$.
(458.1 eV) (Fig. 2(b)). Fifth, Ti–C substitution creates stresses (circle, Fig. 3(a) and (b)) and charges redistribute (Fig. 3(c) and (d)).

Fig. 4(a) displays the σ profiles of pure oxide (red), TC$_{0.1}$ (blue), TC$_{0.5}$ (green), TC$_1$ (pink) and TC$_{10}$ (yellow) at 300–523 K. We find that the improvement reaches one order of magnitude for TC$_{0.1}$, TC$_{0.5}$ and TC$_1$ and $\sigma \propto T$ was attributed to the Boltzmann energy ($k_B T$) created carriers in the CNTs. For TC$_{10}$, $\sigma$ increases by two orders of magnitude relative to the oxide alone, confirming $\tau \sim f_{\text{CNT}} = 10$ wt%. Two factors contribute to the $\sigma$ enhancement according to equation $\sigma = n e^2 \eta/m^* \tau$ where $\eta$ is the mean free path controlled relaxation time. Apparently, the $\eta$ prevails and $n$ increases because the carbon doping was limited. First, pure oxide has an $E_g$ of 3.03 eV at the $\Gamma$ point and doping created an n-type state that lies at 2.674 eV (Fig. 4(b)). At 300 K, $k_B T (= 0.0259$ eV) was 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 $k_B T \propto \Delta E_{d-c} < \Delta E_{v-d} < \Delta E_{v-c}$ remains at 523 K ($k_B T_{523K} = 0.045$ eV), indicative of unchanged $n$. Third, the UV-vis spectra support calculation and $E_g$ was 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 300 K and 523 K (Table 1 & Fig. 5(a)). Fourth, $S$ was promoted from 470 $\mu$V K$^{-1}$ (oxide) to 550 $\mu$V K$^{-1}$ (TC$_{0.1}$–1) at 300 K and from 500 $\mu$V K$^{-1}$ to 610 $\mu$V K$^{-1}$ at

Table 1  $E_g$ at various $f_{\text{CNT}}$ in comparison with the 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>
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</table>

Fig. 3 The ab initio simulated structure of pure oxide (a) and carbon doped oxide (b) and the corresponding Mulliken charge dispersion of the oxide (c) and doped oxide (d).

Fig. 4 The $\sigma$ profiles of the oxide and doped oxide at elevated $T$ (a) and the simulated band profile of the doped oxide (b).

Fig. 5 The UV-vis spectra (a) and $S$ profiles (b) for the oxide and its composites.
Table 2 TEP parameters of TC0.1 in comparison with the reported data at room temperature a

<table>
<thead>
<tr>
<th>Samples</th>
<th>TEP</th>
<th>σ [S cm⁻¹]</th>
<th>S [µV K⁻¹]</th>
<th>αS² [µW m⁻¹ K⁻²]</th>
<th>k [W m⁻¹ K⁻¹]</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs(0.5wt%)/Bi₂Te₃ 23</td>
<td></td>
<td>200 (−50%)</td>
<td>231.2 (65.1%)</td>
<td>1069 (36.4%)</td>
<td>1.20 (−13%)</td>
<td>0.27 (56.81%)</td>
</tr>
<tr>
<td>MWCNTs(0.75wt%)/WS₂ a</td>
<td></td>
<td>3 (12300%)</td>
<td>510 (−22%)</td>
<td>68.4 (7330%)</td>
<td>3.3 (−43.1%)</td>
<td>6.21 × 10^{-3} (127831%)</td>
</tr>
<tr>
<td>Graphene(3wt%)/PbTe 24</td>
<td></td>
<td>234 (1021%)</td>
<td>200 (−46.67%)</td>
<td>936 (289%)</td>
<td>0.93 (−51.8%)</td>
<td>0.3 (602%)</td>
</tr>
<tr>
<td>Graphene(2.5wt%)/CulnTe₂ 25</td>
<td></td>
<td>30 (10.42%)</td>
<td>240 (−5.88%)</td>
<td>173 (−2.26%)</td>
<td>3.823 (−1.29%)</td>
<td>1.36 × 10^{-2} (−1.02%)</td>
</tr>
<tr>
<td>TC0.1</td>
<td></td>
<td>0.71 (4249%)</td>
<td>552.8 (14%)</td>
<td>21.5 (5353%)</td>
<td>2.43 (−24.8%)</td>
<td>3.04 × 10^{-3} (7380%)</td>
</tr>
</tbody>
</table>

 a The numbers in brackets denote an increase in % with respect to the initial and negative sign indicates a negative enhancement.
The (100) and (010) planes, accounting for the increased $S$ decreases towards a positive regime. Tube addition creates a lengthening of the mean free path and $m^*$ change upon tube addition. The weak tube-oxide coupling induces interfacial scattering and results in reduced $k$. $S$ was negative at a low $f_{CNT}$ and increases from $T_C0.1$ to $T_C1$. $T_C10$ was governed by p-type CNTs and $S$ decreases towards a positive regime. Tube addition creates a doped state below LUMO and $m^*/m_o$ increases by 61–62% along the (100) and (010) planes, accounting for the increased $S$.

### Conclusions

CNTs/TiO$_2$ composites made using an SPS technique exhibit increased $\sigma/k$ and $S$, and the underlying mechanism involves the lengthening of the mean free path and $m^*$ change upon tube addition. The weak tube-oxide coupling induces interfacial scattering and results in reduced $k$. $S$ was negative at a low $f_{CNT}$ and increases from $T_C0.1$ to $T_C1$. $T_C10$ was governed by p-type CNTs and $S$ decreases towards a positive regime. Tube addition creates a doped state below LUMO and $m^*/m_o$ increases by 61–62% along the (100) and (010) planes, accounting for the increased $S$.

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### References