Graphene-Au nanoparticle based vertical heterostructures: a novel route towards high- ZT Thermoelectric devices

Zhen-Yu Juang, Chien-Chih Tseng, Yumeng Shi, Wen-Pin Hsieh, Sou Ryuzaki, Noboru Saito, Chia-En Hsiung, Wen-Hao Chang, Yenny Hernandez, Yu Han, Kaoru Tamada, Lain-Jong Li

PII: S2211-2855(17)30357-9
DOI: <http://dx.doi.org/10.1016/j.nanoen.2017.06.004>
Reference: NANOEN2010

To appear in: *Nano Energy*

Received date: 5 March 2017
Revised date: 25 May 2017
Accepted date: 2 June 2017

Cite this article as: Zhen-Yu Juang, Chien-Chih Tseng, Yumeng Shi, Wen-Pin Hsieh, Sou Ryuzaki, Noboru Saito, Chia-En Hsiung, Wen-Hao Chang, Yenny Hernandez, Yu Han, Kaoru Tamada and Lain-Jong Li, Graphene-Au nanoparticle based vertical heterostructures: a novel route towards high- ZT Thermoelectric devices, *Nano Energy*, <http://dx.doi.org/10.1016/j.nanoen.2017.06.004>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Graphene-Au nanoparticle based vertical heterostructures: a novel route towards high-ZT Thermoelectric devices

Zhen-Yu Juang^{*a,b}, Chien-Chih Tseng^c, Yumeng Shi^{c,d}, Wen-Pin Hsieh^e, Sou Ryuzaki^f, Noboru Saito^f, Chia-En Hsiung^c, Wen-Hao Chang^a, Yenny Hernandez^g, Yu Han^c, Kaoru Tamada^f, Lain-Jong Li^{c*}

^a Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan

^b SulferScience Technology Co., Ltd., Taipei 10696, Taiwan

^c Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

^d SZU-NUS Collaborative Innovation Center for Optoelectronic Science & Technology, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, Shenzhen University, Shenzhen 518060, China

^e Institute of Earth Sciences, Academia Sinica, Taipei 11529, Taiwan

^f Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan

^g Department of Physics, Universidad de los Andes, Bogotá 111711, Colombia

Abstract

Monolayer graphene exhibits impressive in-plane thermal conductivity ($>1000 \text{ W m}^{-1} \text{ K}^{-1}$). However, the out-of-plane thermal transport is limited due to the weak van der Waals interaction, indicating the possibility of constructing a vertical thermoelectric (TE) device. Here, we propose a cross-plane TE device based on the vertical heterostructures of few-layer graphene and gold nanoparticles (AuNPs) on Si substrates, where the incorporation of AuNPs further inhibits the phonon transport and enhances the electrical conductivity along vertical direction. A measurable Seebeck voltage is produced vertically between top graphene and bottom Si when the device is put on a hot surface and the figure of merit ZT is estimated as 1 at room temperature from the transient Harman

method. The polarity of the output voltage is determined by the carrier polarity of the substrate. The device concept is also applicable to a flexible and transparent substrate as demonstrated.

Keywords:

thermoelectric, graphene, nanoparticle, heterostructure

Introduction

Thermoelectric (TE) materials have been used for many years to convert the heat into electricity and thus they can help to minimize the waste *heat* released to the environment. The TE conversion efficiency of a bulk material is typically evaluated by the figure of merit (ZT) = $\alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient of the material, σ is the electrical conductivity, κ represents the thermal conductivity, and T is the average temperature of hot and cold sides. Note that the thermal conductivity can be written in the form: $\kappa = \kappa_e + \kappa_L$, where κ_e and κ_L are the thermal conductivities contributed by electrons and phonons respectively. Typically, ZT can be enhanced by either reducing the thermal conductivity κ or increasing the power factor $\alpha^2 \sigma$ of a chosen material. However, the Weideman-Franz law states that the ratio, $\sigma T / \kappa_e$ is a constant.[1] In other words, increasing electrical conductivity accompanies with an unavoidable increase in κ_e . Dresselhaus and Hicks proposed that the dimension change of materials from bulk to nanostructures allows the control over α independently [2, 3] because κ_L can be significantly lowered when the dimension of materials is close to the phonon wavelength (tens to hundreds of nanometers), enabling efficient scattering of phonons during the heat transport processes[2]. Therefore, the ZT is no longer limited by the intrinsic properties of bulk materials and could be improved by the decrease in κ .

Reducing thermal conductivity of a chosen material with a high power factor is a widely used strategy for achieving high ZT . However, the synthesis of nanostructural TE materials may be complicated and costly.[4] In this paper we take an alternative approach, where we start from a material with low thermal conductivity and then enhance its power factor. Monolayer 2D materials such as graphene have attracted global attention because of its impressive in-plane physical and chemical properties.[5, 6] On the contrary the cross-plane thermal conductivity is as low as $< 10 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ of pyrolytic graphite.[7, 8] In other words, the intrinsic low cross-plane thermal conductivity is beneficial for constructing TE devices with a high ZT if the cross-plane electrical conductivity (or power factor) can be enhanced. So far, the applications based on its out-of-plane properties have been rarely reported. Here, we demonstrate a new TE device concept by integrating the bottom Si (or plastic substrate) with the surface heterostructures; i.e. few-layer graphene (FLG) intercalated with Au nanoparticles (AuNPs). The high-quality and large lateral sized monolayer graphene up to few inches is synthesized by the scalable chemical vapor deposition (CVD) method, and both the graphene and 1-dodecanethiol $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ (DDT) stabilized gold nanoparticles (DDT-AuNPs) can be transferred onto arbitrary bottom substrates[9, 10] in a layer-by-layer manner. The phonon transport from one graphene layer to another through DDT-AuNPs will be restricted since the Au nanoparticle size is comparable to the phonon wavelengths; however, electrons could still pass through DDT-AuNPs easily because the de Broglie wavelength of electrons (around sub-nanometer) is much smaller than the size of DDT-AuNPs. Our experimental results show that the graphene-DDT-AuNPs heterostructures can suppress the overall thermal conduction. Meanwhile, the electrically conductive DDT-AuNPs improve the electrical conductivity. These two

factors together contribute to a measurable Seebeck voltage and enhanced ZT in the proposed vertical TE devices, enabling the use of surface heterostructures for heat harvesting.

Experimental

Growth and transfer of graphene. Single-layer graphene (SLG) films were synthesized by low pressure CVD (LPCVD) in a hot-wall furnace consisting of a 25 mm (inner diameter) quartz tube using commercial oxygen-free copper foil (99.99%, ASTM/UNS no. C10200, 25 μm in thickness) as the catalytic substrates. First, the Cu foil was loaded in the center of the furnace and heated to the reaction temperature 1050 $^{\circ}\text{C}$ under an Ar atmosphere at 10 Torr (flow = 1000 sccm), following by thermal annealing at the same temperature for 40 min in H_2/Ar (50 sccm / 100 sccm). After that, the gas condition was switched to a $\text{CH}_4/\text{H}_2/\text{Ar}$ gas mixture (2 sccm / 50 sccm / 1000 sccm) for 30 minutes to grow graphene. During the cooling, the furnace was cooled to 200 $^{\circ}\text{C}$ with the gas mixture of H_2/Ar (25 sccm / 1000 sccm).

For the transfer of graphene, polymethyl-methacrylate (PMMA) was first spin-coated on SLG/Cu foils at 900 rpm for 15 sec and 2000 rpm for 60 sec. The PMMA/SLG/Cu foil sample was cured on a hot plate at 100 $^{\circ}\text{C}$ for 1 min. After that, the sample was placed in a copper etching solution (0.5M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution) for 4 hrs. After the copper substrate was removed, the PMMA/SLG sample was transferred onto DI water for overnight. Finally, the floating PMMA/SLG was transferred to the target substrate followed by slow spinning to dry the sample, during which the surface wrinkles of the PMMA/SLG will be flattened due to the spinning. After the planarization, PMMA can be removed by acetone washing.

Preparation and spin-coating of Au Nanoparticles. Toluene dispersion of Didodecyldimethylammonium bromide (DDAB; 100 mM) was first prepared. 100 mg Tetrabutylammonium borohydride (TBAB) and 40.6 mg HAuCl_4 were dispersed into 4 mL DDAB solution. 172 mg of Decanoic acid (DA) and 2 μL of 1-dodecanethiol were dispersed into 10 mL and 2 mL toluene, respectively. DA solution and TBAB solution were mixed in a three-necked flask and stirred, followed by the addition of HAuCl_4 solution. After the color of the solution changed to red, 1-dodecanethiol solution was injected into it, and the solution was stirred for overnight. The solution was then heated in oil bath for one hour at 100 $^{\circ}\text{C}$. The toluene dispersion of the AuNPs capped with 1-dodecanethiol (DDT-AuNPs) was centrifuged (15 $^{\circ}\text{C}$, 12000 rpm, 10 min) together with 10 mL ethanol to remove the excess organic compounds. Precipitated Au nanoparticles (AuNPs) were dispersed into 5 mL chloroform and centrifuged again with 10 mL ethanol at the same condition. Finally, the DDT-AuNPs precipitates were dispersed into chloroform.

For the deposition of DDT-AuNPs on target substrates, 1 mg powders of DDT-AuNPs were first dissolved in 10 mL Chloroform at room temperature. The solution exhibits a purple color. A spin-coating method was used for the deposition of DDT-AuNPs clusters. The substrate was placed

on a spin-coater to form a uniform distributed AuNPs clusters with a two-step process (900 rpm for 15 sec followed by 7000 rpm for 30 sec).

Transient Harman's method for the measurement of figure of merit (ZT). The ZT values of the samples were measured using reported transient Harman's method (THM).[11] Theoretically the ZT should be measured in an adiabatic condition. Thus we preform the measurements of THM in a vacuum chamber consisting a polytetrafluoroethylene (low κ of $0.25 \text{ Wm}^{-1}\text{K}^{-1}$) sample holder with thin gold foils as the electrodes (thickness $< 1 \mu\text{m}$) and the electrical data was collected by a high-accuracy multi-meter (KEYSIGHT B2961A power source). The experimental configuration can minimize the heat transfer to or from the measurement system. TE samples with various layer numbers were first placed on the PTFE sample holder and then loaded into the vacuum chamber followed by pumping down to the background pressure (5 mTorr). After the pressure reached to 5 mTorr, a current source of $5 \mu\text{A}$ was applied to the samples and then monitored their voltage profile. The measurement set-up is illustrated in Figure 1.

Time-domain thermoreflectance (TDTR) method for thermal conductance G measurement.

Time-domain thermoreflectance (TDTR) is an ultrafast optical pump-probe technique which utilizes the output of a femtosecond Ti:sapphire laser to pump and probe the ultrafast dynamics of thermal diffusion through the materials, and thus the thermal conductance G could be estimated. An Au film with a thickness around 100 nm was first coated on the surface of the graphene/DDT-AuNPs/Si sample. In TDTR measurements, the output of the laser was split into a pump beam and a probe beam. The pump beam was modulated at 8.7 MHz and heated the surface of Au film to create temperature variations. The probe beam then measured the resulting changes in the optical reflectivity of Au surface due to the temperature changes on the Au film. The in-phase V_{in} and out-of-phase V_{out} components of the variations of the reflected probe beam intensity were measured by a Si photodiode and a lock-in amplifier. To determine the interface thermal conductance G , we compared the ratio $V_{\text{in}}/V_{\text{out}}$ of the output of the lock-in amplifier as a function of delay time between the pump and probe beams to calculations using a thermal model that simulates the dynamics of heat flow in our samples.

Figure 1. Design of the system for measuring ZT using transient Harman's method. A home-built sample holder was made from polytetrafluoroethylene. The top and bottom electrodes were fabricated using thin gold foils. The sample holder encloses the sample in a dark environment and the electrodes of thin gold foils keep the heat loss minimum while maintaining good electrical contact to samples.

Results

Structure of the cross-plane thermoelectric devices. Figure 2a shows the schematic diagram of the cross-section for the cross-plane thermoelectric TE device based on one DDT-AuNPs layer and one graphene layer on a highly doped *p*-type Si substrate. The DDT-AuNPs were first dissolved in chloroform and spin-coated on a Si substrate followed by transferring a layer of graphene monolayer on top. The DDT-AuNPs deposition and graphene transfer can be repeated to obtain few-layered heterostructures (as shown in Figure S1). The details of the synthesis of graphene and DDT-AuNPs are described in Methods. Finally, a gold thin film with a thickness of 100 nm was coated on the surface of top layer graphene as a top contact layer. Figure 2b shows the AFM image of as-coated DDT-AuNPs layer on the Si substrate before graphene transfer. The average coverage of the DDT-AuNPs is estimated as 71.4 % from AFM image analysis. Figure 2c is the cross-sectional height profile along the line indicated in Figure 2b, and the result suggests that the height of DDT-AuNPs layer is about 8 nm, slightly larger than the diameter 5-7 nm observed in TEM image (Figure 2d). This suggests that the AuNPs are well dispersed and deposited on Si substrates. Raman spectrum for the monolayer graphene in Figure 2e shows a pronounced 2D band at 2694 cm^{-1} , a peak intensity ratio (2D band/G band) of 3.1, and a weak D band at 1360 cm^{-1} , suggesting that the graphene is a monolayer with a low defect density.[10]

Figure 2 Characterizations of AuNPs and graphene for the TE devices. (a) The schematic diagram of one graphene/DDT-AuNPs layer on a substrate. (b) The AFM image of as-prepared DDT-AuNPs layer on substrate. (c) The AFM line-scan from (b). (d) TEM image of DDT-AuNPs. (e) Raman spectrum of a monolayer graphene (excitation wavelength 532 nm) .

Cross-plane conduction of charge carriers and phonons. To prove that graphene is thermal resistive along the cross-plane direction, Figure 3a shows the thermal image of the sample with three graphene layers (with the size $7 \times 7 \text{ cm}^2$) on a 4-inch Si wafer, where the sample was heated by a hot-plate (set at 70°C). The temperature distribution detected by the thermal detector displays significant differences between the area with and without graphene on top. Due to that graphene is nearly invisible to IR camera, the center part of the wafer (with 3 layer graphene) reflects the temperature of silicon. The higher temperature at the area covered with graphene indicates that the graphene layers exhibit the outstanding cross-plane thermal resistance. The operation of vertical TE devices relies on the control of out-of-plane charge carrier. In principle, the charge transport from the bottom substrate to the top layer graphene should be easier through the bridging DDT-AuNPs. To reveal the effects of DDT-AuNPs on the carrier conduction path, conductive AFM (c-AFM) was used to reveal the spatial map of the vertical conduction. Figure 3b shows the typical AFM topography image of the graphene/DDT-AuNPs/Si sample, and Figure 3c is the corresponding c-AFM image of the same area as in Figure 3b. The bright area in Figure 3b, corresponding to the area with the presence of AuNPs, matches well to the high conduction area in Figure 3c, indicative of preferential electron transport through the AuNPs.[12, 13] Since gold is an excellent electrical conductor, the heat conduction through electron transport should still remain to

contribute to the out-of-plane thermal conductivity. Hence, it is useful to investigate whether the other thermal transport (phonon transport) can be significantly suppressed with the intercalated DDT-AuNPs. The measurement of cross-plane thermal conductance G of the graphene/DDT-AuNPs samples at room temperature was conducted using time-domain thermoreflectance (TDTR).^[14] TDTR method is an ultrafast optical pump-probe technique which utilizes the output of a femtosecond Ti:sapphire laser to pump and probe the ultrafast dynamics of thermal diffusion through the materials (details in Method). Figure 3d compiles the results of thermal conductance measured by TDTR, where the square data-point at $70 \text{ MW}\cdot\text{m}^{-2}\text{K}^{-1}$ is the thermal conductance between the top gold electrode and the Si substrate (without graphene/DDT-AuNPs in between) as the reference. The dotted-line at $25 \text{ MW}\cdot\text{m}^{-2}\text{K}^{-1}$ represents the cross-plane thermal conductance of monolayer graphene from a previous report.^[8] Figure 3d shows that the thermal conductance of the devices without DDT-AuNPs (circles) significantly decreases with the increasing number of graphene layers. The G for the devices with DDT-AuNPs (triangles) are apparently lower than those without DDT-AuNPs in all cases (1 or 2 or 3 graphene layers), suggesting that DDT-AuNPs effectively suppress the vertical phonon transport.

Figure 3 Cross-plane charge carrier and phonon conduction. (a) The thermal image of three graphene layers with the size of $7 \times 7 \text{ cm}^2$ on a 4-inch Si wafer. Points A and C, the positions within graphene area, exhibited higher temperature than that of the points B and D beyond the graphene area (see supporting Figure S2 for the detail of experimental setup). (b) The AFM image of 1-layer graphene/DDT-AuNPs sample. (c) The corresponding conductive AFM image of (b). (d) The thermal conductance of Au/Si, graphene/DDT-AuNPs/Si and graphene/Si samples measured by TDTR method. Each data point was the average of at least 3 samples (or locations).

When a temperature difference has been generated along the vertical direction, both phonons and electrons will thermodynamically diffuse from the hot to the cold sides. Our results on graphene/DDT-AuNP/Si heterostructural devices suggest that during this diffusion process some phonons are blocked by the graphene/DDT-AuNPs heterostructure along the vertical directions. Note that the suppression of phonon diffusion may be contributed by several factors: (i) the phonon scattering from DDT-AuNPs; (ii) The presence of capping molecules DDT surrounding AuNPs, where the organic molecules normally exhibit low thermal conductivity.[15] Even though the electron transport is enhanced by AuNPs, the blocking of phonon transports by DDT or AuNPs seems to be more pronounced; thus the overall thermal conduction is reduced with the incorporation of DDT-AuNPs in our vertical TE devices.

Estimation of ZT for graphene/DDT-AuNPs/Si heterostructures. The ZT estimation for bulk TE materials requires separate measurements for α , σ , κ and T . However, for the nanomaterials in a hybrid system, it is hard to measure these parameters with acceptable accuracy. Hence, the transient Harman method (THM) was employed.[11] We constructed a test platform consisting of a vacuum chamber and a high-performance source/meter KEYSIGHT® B2962A with a high sampling rate of 10 μ s. Note that a high sampling rate is crucial for THM because the thermoelectric response is extremely fast in such thin heterostructures.[4] All the samples were measured in a vacuum environment of $\approx 10^{-3}$ Torr to approximate the adiabatic condition. This is necessary because of the adiabatic condition is the basic requirement for THM (see Experimental). In addition, a specially designed sample holder provides a dark environment and thus the plasmon assisted thermal or electrical effect could be neglected.[16] The electrodes of thin gold foils keep the minimum heat loss with good contact with sample. We have also measured the ZT for a commercial TE device based on Bi_2Te_3 using THM and the measured ZT value 0.5 is consistent with the specification ($ZT = 0.5 - 1$, depends on the doping concentration) of the TE device (see supporting Figure S3 for details).

Figure 4a shows the schematic diagram of the TE device used for THM, and inset is the photo of an actual sample with a size of $10 \times 10 \text{ mm}^2$, where the top surface was coated with a thin gold film as a top electrode. Based on the theory of Peltier effect and Fourier's law, the ZT could be directly measured by applying a transient direct current vertically across the device and recording the voltage-to-time (V - t) response. The inset in Figure 4b shows the typical V - t curve observed when the transient current is turn on (at $t = 2 \text{ ms}$) and off (at $t = 4 \text{ ms}$). When the applied current was shut down, the voltage-to-time response could be separated into two regions: a linear voltage drop (from point A to B in inset) followed by an exponential voltage drop (curve BC in inset). The linear region obeys the Ohm's law and gives the voltage drop V_R , and the exponential component represents the Seebeck voltage of the sample and gives another voltage drop V_α as show in Figure 4b, where a turning point dividing these two regions can be determined as indicated by the red circle (see supporting Figure S4 for details). The voltage drop of these two regions is used to

estimate ZT by the equation $ZT = V_{\alpha}/V_R$ from the THM.[1] The typical result for a 3-layer graphene/DDT-AuNPs/Si sample shown in Figure 4b indicates that the ZT for the vertical TE device is about 1. Note that the voltage spike at $t \approx 4.0$ ms is due to the momentary inductive coupling between the current and voltage circuits.[4] This spike only appears within the time scale $< 50\mu\text{s}$ after voltage drop in our measurements. Note that the supporting Figure S5 shows that the V - t response of the reference device Au deposited on Si exhibits nearly no voltage drop V_{α} but dominated by the slight RC delay, where the voltage decay time of RC delay (< 0.2 ms) is much shorter than that of V_{α} (~ 1 ms in Figure 4b). Figure 4c summarizes the obtained ZT values for the devices with 1, 2, or 3 graphene layers transferred on top of Si with or without DDT-AuNPs intercalation. The ZT of bulk silicon at 300 K is approximately 0.01.[17] The ZT for the sample without DDT-AuNPs intercalation slightly increases with the number of graphene layers ranging from $ZT \approx 0.1$ to 0.3. When the gaps between graphene layers are intercalated by DDT-AuNPs, the ZT value increases significantly. The device with 3 graphene layers and DDT-AuNPs exhibits a ZT value as high as 1.0 as shown in Figure 4b.

Figure 4 Transient Harman method to estimate ZT . (a) The schematic diagram of the TE device used for THM. The inset shows the photo of an actual sample with a size of $10 \times 10 \text{ mm}^2$, where the top surface was coated with a thin gold film as electrode. (b) The typical voltage-to-time response measured by transient Harman method. A turning point can be determined as indicated by the red circle. (c) The measured ZT vs. number of graphene layers on Si substrate with and without DDT-AuNPs. Each data point was the average of 4 separate samples.

Discussion

To understand why the ZT increases with the number of DDT-AuNPs/graphene layers, we measure the Seebeck coefficient and estimate the Ohmic resistance of the TE devices. The dependence of output voltage and temperature for the samples with different numbers of graphene/DDT-AuNPs layers are shown in Figure 5a, where the Seebeck coefficients can be determined by the slope. Figure 5b summarizes that the Seebeck coefficient significantly increases with the number of DDT-AuNPs/graphene layers ranging from 146 to $350 \mu\text{V/K}$. This result may be explained by that the

concentration of temperature-driven charge carriers decreases with the increase in number of layers.[18] However, the decrease of charge carrier concentration also results in the reduction of electrical conductivity. In other words, the effects of charge carrier concentration on Seebeck coefficient and electrical conductivity are mutually competitive.[18] The resistance of the TE device may be estimated from the voltage v.s. current response in the linear region (mentioned in Figure 4b) after the applied current was shut down. Using this approach, the resistance for the TE devices without DDT-AuNPs for 1-layer graphene is 560 Ohm and it increases to 973 Ohm for 3-layer graphene as shown in supporting Figure S6. The TE devices with DDT-AuNPs exhibit lower resistance, where the 1 DDT-AuNPs/graphene layer is 158 Ohm and it increases to around 231 Ohm for 2 and 3 DDT-AuNPs/graphene layers. In addition to the increase in Seebeck coefficient, Figure 5b also compiles the thermal conductance obtained in Figure 3c, where the thermal conductance of the Au/DDT-AuNPs/graphene/Si TE devices decreases from $22 \text{ MW}\cdot\text{m}^{-2}\text{K}^{-1}$ (1 DDT-AuNPs/graphene layer) to the $15 \text{ MW}\cdot\text{m}^{-2}\text{K}^{-1}$ for both 2 and 3 DDT-AuNPs/graphene layers. In brief, the low cross-plane thermal conductivity and increased cross-plane Seebeck coefficient (as well as the power factor) contribute to the enhanced ZT value for the devices with more DDT-AuNPs/graphene layers.

Figure 5 Seebeck coefficient and thermal conductance (a) The plot of the output voltage vs. temperature difference of the samples with different numbers of graphene/DDT-AuNPs layer. (b) The Seebeck coefficient (solid squares) and thermal conductance (empty squares) vs. number of graphene/DDT-AuNPs layers.

With the ultra-thin feature, 2D materials exhibit excellent transparency and flexibility, which allow 2D material-based TE devices to function in specific environments. For example, transparent TE

devices could be applied on windows of building/vehicles because significantly large temperature gradient always presents between the interior and exterior surfaces of windows. The flexible TE device could be applied on the heat sources with uneven surfaces such like human skin. The inset in Figure 6a shows the photo of 2-layered graphene/DDT-AuNPs stacks transferred onto an *n*-type indium-tin-oxide (ITO) film which was coated on a transparent flexible polyethylene terephthalate (PET) substrate. The area of graphene/DDT-AuNPs is $30 \times 30 \text{ mm}^2$ and the transmittance can be estimated as $\approx 60 \%$ at the wavelength of 550 nm. The output of a high Seebeck voltage for this device is shown in Figure 6b, demonstrating the feasibility of constructing transparent and flexible TE devices using the heterostructural approach.

A complete TE device typically contains TE couples consisting of *n*- and *p*-type elements connected thermally in parallel and electrically in series.[18] The traditional way to manipulate the polarity of the TE device is to perform *n*- or *p*-doping to the TE materials. For our vertical TE devices, we observe that the polarity strongly depends on the doping density of the substrates. For example, when a *p*-type Si is used as the substrate (as in Figure 4a), the Seebeck voltage increases with the temperature difference. By contrast, the negative Seebeck voltage-temperature dependence is observed if an *n*-type substrate is adopted (Figure 6). The *ZT* of the sample in Figure 6 is around 0.2 determined by THM (Supporting Figure S7). This feature of manipulating device polarity by choosing an appropriate substrate is beneficial for the production of future cross-plane TE devices.

Figure 6 (a) The 2-layered graphene/DDT-AuNPs on indium-tin-oxide (ITO) coated transparent flexible polyethylene terephthalate (PET) substrate. The area of graphene/DDT-AuNPs is $30 \times 30 \text{ mm}^2$. The transmittance can be estimated as $\approx 60 \%$ at 550 nm of wavelength. (b) The negative voltage output vs. temperature difference of the sample in (a).

Conclusion

We demonstrate a new concept of TE devices, where the substrate surface is covered by graphene/DDT-AuNPs layer heterostructures to lower the phonon transport, leading to lower thermal conductivity along the vertical direction. Also, the incorporation of electrically conductive AuNPs improves the electron transport. Therefore, the low cross-plane thermal conductivity together with the increased cross-plane Seebeck coefficient (as well as the power factor) contribute to the high ZT value of the proposed devices. We demonstrate that the TE device based on three-layer graphene/DDT-AuNPs/*p*-Si achieves a high $ZT > 1$ along the cross-plane direction at room temperature, in clear contrast to most commercial TE devices ($ZT < 1$). The polarity of these vertical TE devices is determined by the substrate carrier type, indicating that the full devices may be constructed on Si or ITO using microelectronic compatible processes. The TE device concept provided here is not only limited to the selected graphene or AuNPs. We expect that the performance of the TE devices based on heterostructures could be further optimized by using other potential 2D and cheaper intercalated materials such as fullerenes.[19, 20] Although the research is still in their infancy, this report demonstrates the proof-of-concept TE devices which may be suitable for recycling wasted heat from hot surfaces.

Acknowledgement

This work was supported by the Ministry of Science and Technology of Taiwan under Contract No. MOST 104 – 2112 – M – 006 – 001, MOST 103-2112-M-001 -001 -MY3 and MOST 104-2112-M-001 -045. L.J.L, C.C.T, Y.S acknowledge the support from King Abdullah University of Science and Technology. Y.S. acknowledges the support from the Thousand Young Talents Program of China, the National Natural Science Foundation of China (Grant No. 51602200) and Educational Commission of Guangdong Province (Grant No. 2016KZDXM008). This project was supported by Shenzhen Peacock Plan (Grant No. KQTD2016053112042971).

References

- [1] H.J. Goldsmid, Introduction to Thermoelectricity, Springer 2009.
- [2] M.S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, P. Gogna, Advanced Materials, 19 (2007) 1043-1053.
- [3] L.D. Hicks, M.S. Dresselhaus, Physical Review B, 47 (1993) 12727-12731.
- [4] R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'Quinn, Nature, 413 (2001) 597-602.

- [5] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science*, 306 (2004) 666-669.
- [6] A.C. Ferrari, F. Bonaccorso, V. Fal'ko, K.S. Novoselov, S. Roche, P. Boggild, S. Borini, F.H.L. Koppens, V. Palermo, N. Pugno, J.A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhanen, A. Morpurgo, J.N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G.F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A.N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G.M. Williams, B. Hee Hong, J.-H. Ahn, J. Min Kim, H. Zirath, B.J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I.A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupesinghe, P. Hakonen, S.R.T. Neil, Q. Tannock, T. Lofwander, J. Kinaret, *Nanoscale*, 7 (2015) 4598-4810.
- [7] A.A. Balandin, *Nat Mater*, 10 (2011) 569-581.
- [8] Y.K. Koh, M.-H. Bae, D.G. Cahill, E. Pop, *Nano Letters*, 10 (2010) 4363-4368.
- [9] X.S. Li, W.W. Cai, J.H. An, S. Kim, J. Nah, D.X. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, *Science*, 324 (2009) 1312-1314.
- [10] A.-Y. Lu, S.-Y. Wei, C.-Y. Wu, Y. Hernandez, T.-Y. Chen, T.-H. Liu, C.-W. Pao, F.-R. Chen, L.-J. Li, Z.-Y. Juang, *RSC Advances*, 2 (2012) 3008-3013.
- [11] T.C. Harman, *Journal of Applied Physics*, 29 (1958) 1373-1374.
- [12] C. Kergueris, J.P. Bourgoin, S. Palacin, *Nanotechnology*, 10 (1999) 8.
- [13] N. Toshima, N. Jiravanichanun, H. Marutani, *Journal of Electronic Materials*, 41 (2012) 1735-1742.
- [14] D.G. Cahill, W.K. Ford, K.E. Goodson, G.D. Mahan, A. Majumdar, H.J. Maris, R. Merlin, S.R. Phillpot, *Journal of Applied Physics*, 93 (2003) 793-818.
- [15] C.L. Yaws, *Transport Properties of Chemicals and Hydrocarbons*, Elsevier Science 2014.
- [16] M. Toma, K. Toma, K. Michioka, Y. Ikezoe, D. Obara, K. Okamoto, K. Tamada, *Physical Chemistry Chemical Physics*, 13 (2011) 7459-7466.
- [17] L. Weber, E. Gmelin, *Applied Physics A*, 53 (1991) 136-140.
- [18] G.J. Snyder, E.S. Toberer, *Nat Mater*, 7 (2008) 105-114.

[19] C. Wan, X. Gu, F. Dang, T. Itoh, Y. Wang, H. Sasaki, M. Kondo, K. Koga, K. Yabuki, G.J. Snyder, R. Yang, K. Koumoto, *Nat Mater*, 14 (2015) 622-627.

[20] P.T. Yin, S. Shah, M. Chhowalla, K.-B. Lee, *Chemical Reviews*, 115 (2015) 2483-2531.

Highlights

We demonstrate a new TE device based on the vertical heterostructures of few-layer graphene, intercalated gold nanoparticles and Si substrates

The incorporation of gold nanoparticles lowers the phonon transport and enhances the electrical conductivity along vertical direction.

The figure of merit ZT is estimated as 1 at room temperature.

The polarity of the output voltage is determined by the carrier polarity of the substrate.

The device concept is applicable to a flexible and transparent substrate as demonstrated.