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Thermoelectric properties of individual single-crystalline PbTe nanowires grown by a vapor transport method

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Abstract
We report the thermoelectric performance of individual PbTe nanowires with sizes ranging from 76 to 436 nm grown from a vapor transport method that synthesizes high-quality, single-crystalline PbTe nanowires. Independent measurements of temperature-dependent Seebeck coefficient (S), thermal conductivity (κ) and electrical conductivity (σ) of individual PbTe nanowires were investigated. By varying the nanowire size, the simultaneous increase and decrease of S ($-130\ \mu$V K^{-1}) and κ (1.2 W m^{-1} K^{-1}), respectively, are achieved at room temperature. Our results demonstrate the enhanced thermoelectric properties of individual single-crystalline PbTe nanowires, compared to that of bulk PbTe, and can provide guidelines for future work on nanostructured thermoelectrics based on PbTe.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

As lead telluride, PbTe, has been the subject of particular attention as a thermoelectric material due to its high ZT [1–13], many efforts have been made to improve thermoelectric properties of PbTe and its alloys, and thus increase the thermoelectric conversion efficiency. The thermoelectric efficiency is given by $ZT = S^2\sigma T/\kappa$ (S is thermopower, σ is electrical conductivity, κ is thermal conductivity and T is temperature), and S, σ and κ are not mutually exclusive. There are a variety of techniques for increasing the thermoelectric efficiency, particularly in nanoscale architectures [14–21]; these strategies are (1) utilizing sharp peaks of the density of electronic states in quantum-sized systems and (2) optimizing of the phonon dynamics to reduce κ in nanostructured systems [22, 23]. In the latter case, which is more practical, the rational incorporation of phonon-scattering elements at several length scales was found to be crucial in decreasing κ significantly [23]. These strategies benefit mostly from using one-dimensional nanowire architectures.

However, measuring κ, σ and S on the same nanowire to obtain ZT is still challenging because each measurement needs a different set of device platforms. As an alternative, one can separately measure κ, σ and S on different nanowires of similar dimension whose physical properties, i.e. carrier concentrations, do not vary significantly. This approach can provide thermoelectric properties of nanowires that can be compared with those of bulk materials, and be an initial

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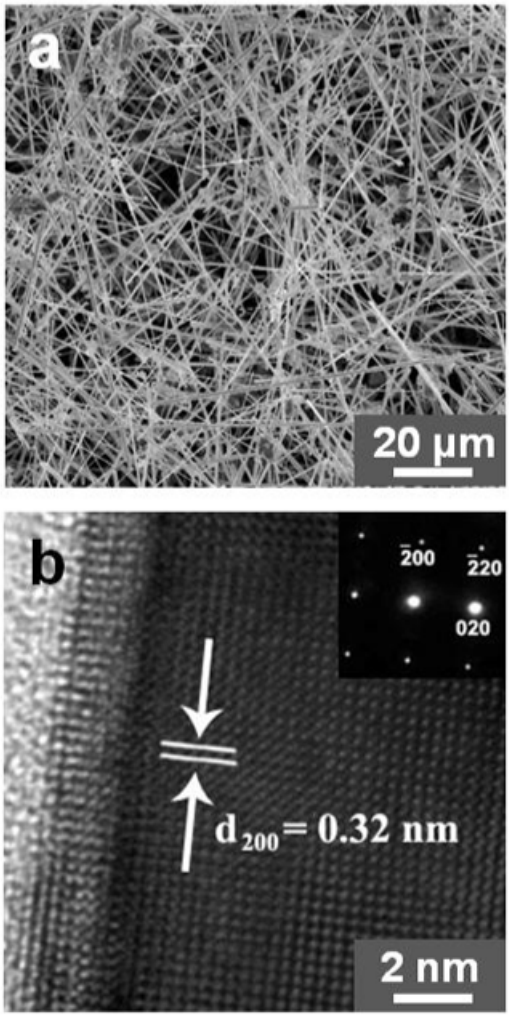

Figure 1. Structural characteristics of single-crystalline PbTe nanowires. (a) A SEM image shows the high-density PbTe nanowires and (b) a lattice-resolved TEM image of an individual nanowire reveals the highly crystalline (200) PbTe planes. The SAED pattern (at the [001] zone axis) confirms that the single-crystalline nanowires grew in the [200] direction (inset).

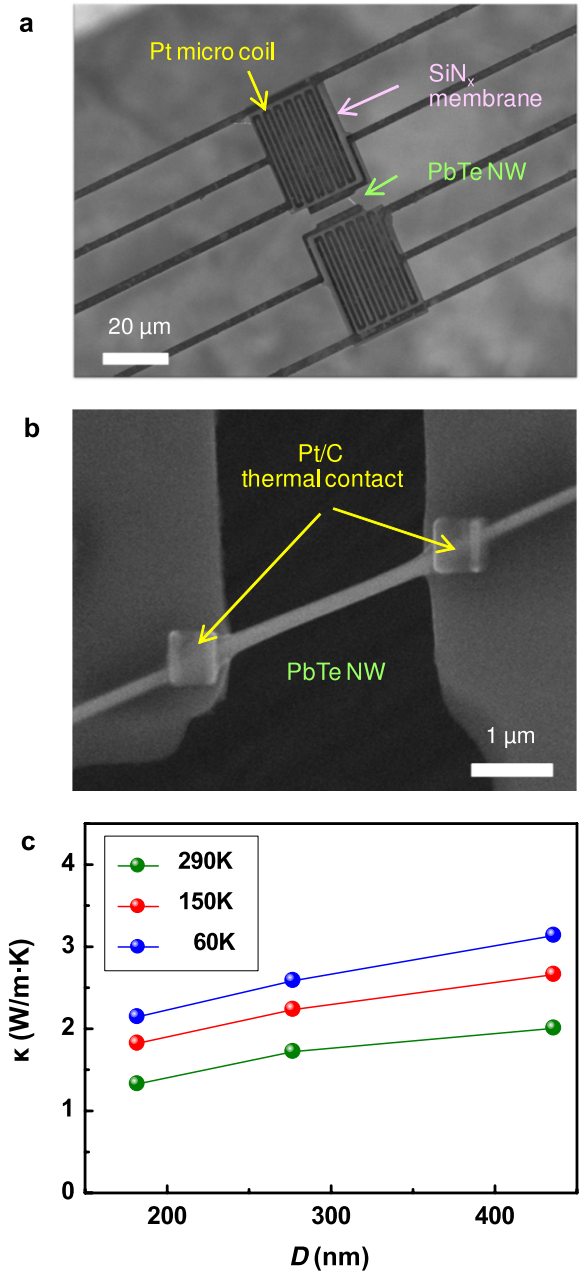

Figure 2. Thermal conductivity of individual PbTe nanowires. (a) An SEM image of a PbTe nanowire bridging two suspended heating membranes for thermal conductance measurement. (b) The highlighted SEM image of a thermal contact between the membrane and PbTe nanowire. (c) Diameter-dependent thermal conductivity of individual PbTe nanowires. The temperatures are 60, 150 and 290 K, respectively.

step toward investigating an increase of the thermoelectric efficiency. Herein, we report the independent measurements of κ, σ and S for individual PbTe nanowires grown from a vapor transport method that synthesizes high-quality, single-crystalline nanowires. The simultaneous increase and decrease of S and κ, respectively, were observed at room temperature.

2. Experimental details

For the synthesis of PbTe nanowires, lead (II) chloride ($PbCl_2$, 99.999%, Aldrich) and tellurium (Te, 99.8%, Aldrich) powders were placed inside a quartz tube reactor. A thermally oxidized Si(100) substrate on which Au nanoparticles were deposited was positioned at a distance of 10 cm away from the PbTe source. As the source was allowed to evaporate at 1100 °C for 2 h under argon flow (300 sccm), PbTe nanowires were grown on the substrate. In this work, the novel growth method for PbTe nanowires is termed a vapor transport method, based on the vapor–liquid–solid (VLS) mechanism using Au catalytic nanoparticles [24]. Figure 1(a) shows a scanning electron microscope (SEM) image of the PbTe nanowires grown on an Si substrate. The PbTe nanowires were found to grow to several hundred micrometers in length and a few hundred nanometers in diameter. Figure 1(b) exhibits the lattice-resolved transmission electron microscope (TEM) image of a PbTe nanowire, demonstrating its single-crystalline structure. The (200) fringes were found to be separated by a

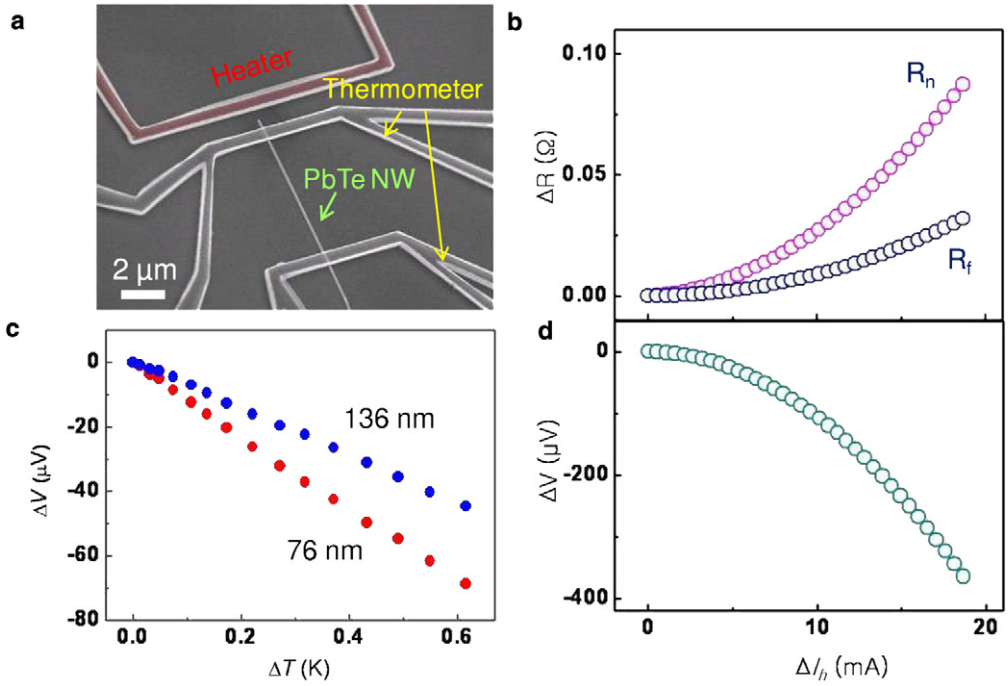

Figure 3. Seebeck coefficient of a PbTe nanowire. (a) A SEM image of a representative device based on an individual single-crystalline PbTe nanowire with $D = 76$ nm for TEP measurements. (b) The graphs show the normalized change in R_n and R_f and thermoelectric voltage as a function of the heater current, I_h, at 300 K. (c) TEPs (S) $= -130$ and -76 μV K^{-1} are obtained from the slope of a linear fit to the data at 300 K.

distance of 3.2 Å, which is equal to that of cubic PbTe crystal ($a = 6.454$ Å).[7] The corresponding selected-area electron diffraction (SAED) pattern, measured on the [001] zone axis, confirmed that the single-crystalline nanowires grew in the [100] direction (inset).

3. Results and discussion

The measurement of κ in individual PbTe nanowires was conducted using a suspended microstructure with two micro-Pt coils that is designed to probe thermal conductance through the PbTe nanowire, while preventing thermal transport through the substrate (figure 2(a)). Two micro-Pt coils patterned on an SiN_x membrane were utilized as a heater and thermometer in the measurement of nanowire thermal conductance. In order to improve the thermal contact between the membrane and the PbTe nanowire, the Pt/C composite was locally deposited using the electron beam of a dual-beam focused-ion-beam (FIB) system (FEI Strata 235), as shown in figure 2(b). κ was calculated from the measured thermal conductance using the PbTe nanowire dimension and the thermal conduction length between thermal contacts. The detailed process for calculating κ using the same suspended microstructure is well described in previous studies [25, 26].

Figure 2(c) shows the diameter (D) dependence of the measured κ data at T of 60, 150 and 290 K. The measured κ decreased as D decreased, and this tendency became more clearly observed as T decreased; the diameter derivatives of the thermal conductivities, $d\kappa/dD$, at temperatures of 290, 150 and 60 K were 2580, 3230 and 3850 kW m^{-2} K^{-1}, respectively. This diameter dependence can be attributed either to the size effects of the nanowires or to the variation in carrier concentrations. Thermal conductivity is given by $\kappa = (1/3)C_v v l$, where C_v is the specific heat per unit volume, v is the phonon group velocity and l is the phonon mean free path. In general, κ depends strongly on l ($\sim 1/T$ due to phonon–phonon scattering) around the Debye temperature ($\Theta_{D,PbTe} \approx 140$ K) [27], because v is essentially insensitive to temperature. The observed κ data in figure 2(c) agrees well with $\kappa \propto 1/T$, as a consequence, $\propto l$; the latter is likely to rely on D at a given T, which implies boundary scattering of phonons in small D. In particular, boundary scattering of phonons seems more obvious at low temperature where both phonon–phonon and phonon–impurity collisions become ineffective. The wavelength of phonons at low temperatures is relatively long and consequently l mostly relies on D. In fact, the observed $d\kappa/dD$ at 60 K exhibited a higher value than those at 150 and 290 K, implying boundary scattering of phonons and a clear diameter dependence of κ at low T. This size effect was also shown by the observation of a peak shift in κ–T [28], where $\kappa \propto T^3$ (entirely from the specific heat C_v) at low T and $\kappa \propto 1/T$ (entirely due to l) at high T. However, it is worth noting that a decreased κ (1.29 W m^{-1} K^{-1} for $D = 182$ nm at 300 K) is only about half that of bulk PbTe. This relatively small reduction in κ is probably due to a short phonon mean free path of PbTe that suppresses the size effect [29].

For the measurement of S, the fabrication, calibration and experimental measurements are described as follows. PbTe

[7] JCPDS card no. 78-1905.

nanowires were dispersed by applying a drop of isopropyl alcohol (IPA) containing free-standing nanowires onto a thermally oxidized Si(100) substrate with a grid of points patterned by photolithography and a lift-off process. The spatial positions and orientations of each nanowire were recorded by digitizing the coordinates from optical microscopy images. A combination of electron-beam lithography and a lift-off process was utilized to fabricate inner micron-scaled Cr (5 nm)/Au (130 nm) electrodes with resistances R_n (near-electrode resistance), R_f (far-electrode resistance) and a microheater connecting a PbTe nanowire on the grid of points. A plasma etching system was used to remove the oxide layer from the outer surface of the nanowires before the deposition of the inner electrodes. The etching and deposition of electrodes were done *in situ* without breaking the vacuum in order to prevent further formation of the oxide layer. Finally, a combination of photolithography and a lift-off process was utilized to fabricate outer electrodes, providing individual PbTe nanowire devices.

Figure 3(a) shows an SEM image of a representative device based on an individual single-crystalline PbTe nanowire with $D = 76$ nm used for thermoelectric power (TEP) measurements. A bias voltage was applied to the heater line in order to produce Joule heating and to raise the temperature locally around the adjacent contact area. The heat generated by the local heater was designed to propagate through a 0.5 μm thick SiO_2 layer, providing a temperature gradient across the PbTe nanowire and the surface of the SiO_2 layer to which it was thermally anchored due to low thermal conductivity ($\sim$0.5 W m^{-1} K^{-1}). The temperature of the nanowire–electrode junctions was monitored by variations in the R_n and R_f electrodes using the four-probe method. The thermoelectric voltages across the PbTe nanowire can be readily measured by the electrode contacts with the nanovoltmeter. As shown in figure 3(b), a heater current (I_h) applied to the heater gives rise to a temperature gradient across the substrate through Joule heating. The temperature difference (ΔT) between the two PbTe nanowire–electrode contacts was obtained by probing the resistance variation (ΔR) of R_n and R_f. As I_h changed, it was found that the difference of ΔR_n and ΔR_f is proportional to I_h^2. The variation in the thermoelectric voltage (ΔV) was also measured across the PbTe nanowire with increasing I_h.

In this work, S of the PbTe nanowire was obtained by the simple relation $S = \Delta V/\Delta T$, since it was confirmed that $\Delta V \propto I_h^2 \propto \Delta T$. Figure 3(c) demonstrates the linearity of the thermoelectric voltages (ΔV) measured with respect to the applied temperature difference (ΔT) for two nanowires at room temperature. S of 76 and 132 nm diameter PbTe nanowires were -130 and -72 μV K^{-1}, respectively. The negative sign of S values indicates that our PbTe nanowires grown by a vapor transport method can be attributed to electron diffusion, indicating that the nanowires are n-type semiconductors. Furthermore, S of small-diameter nanowires (76 nm) is larger than that of large diameter (136 nm), but agrees with the diameter dependence in earlier measurements of S of individual single-crystal antimony telluride (Sb_2Te_3) nanowires [30].

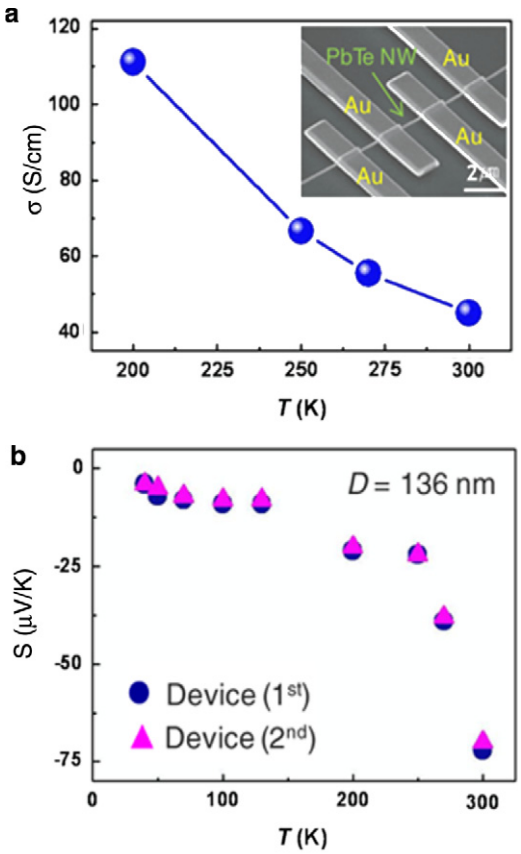

Figure 4. Temperature-dependent electrical conductivity and Seebeck coefficient of n-type PbTe nanowire. (a) Electrical conductivity (σ) of a $D = 140$ nm nanowire was measured by four-probe measurement over the temperature range 200–300 K: the inset shows an SEM image of a four-terminal device based on an individual PbTe nanowire. (b) Seebeck coefficient of a nanowire with $D = 136$ nm was measured in the temperature range 40–300 K (O = first measurement, Δ = second measurement of the same device).

For detailed study, T dependence of σ ($D = 140$ nm) and S ($D = 136$ nm) was investigated for individual PbTe nanowires, as seen in figure 4. Fabrication of a nanodevice with four probes based on the individual PbTe nanowire for measuring σ was described in detail elsewhere [31–34]. From I–V measurements[8], the contacts to the nanowire were observed to be highly ohmic at 300 K, corresponding to a σ of 45 S cm^{-1} that is smaller than that of the bulk (256 S cm^{-1}) [35], which probably arises from surface scattering of charge carriers that reduces σ compared to that of the bulk. While this scattering decreases σ, this loss can be compromised by a decrease in κ and an increase in S. It was found that σ decrease as T increases, which can be ascribed to its doped nanowire composition (degenerate) exhibiting near-metallic conductivity [23]. However, the magnitude of S increases as T increases and tends to zero as T decreases. S is the entropy per electric charge and thus S must go to zero at 0 K [36]. The trend of S in figure 4(b) was relatively temperature-invariant below 200 K. Importantly, S at 290 K

[8] See supporting information available at stacks.iop.org/Nano/22/295707/mmedia.

of the PbTe nanowire with $D = 136$ nm was found to be $-72\ \mu V\ K^{-1}$ that is about three times larger than that of bulk PbTe ($S \approx -25\ \mu V\ K^{-1}$) [37].

4. Conclusions

In summary, we separately measured κ, σ and S for individual PbTe nanowires and observed the enhanced thermoelectric properties, compared with those in bulk PbTe at room temperature. Based upon the result of κ (1.29 $W\ m^{-1}\ K^{-1}$, $D = 182$ nm), σ (45 $S\ cm^{-1}$, $D = 140$ nm) and S ($-72\ \mu V\ K^{-1}$, $D = 136$ nm) at 300 K, the experimental estimation of ZT in PbTe nanowires is ~0.0054, while ZT in bulk PbTe is approximately ~0.002 at 300 K. Such an enhanced ZT can in part be attributed to the size effect of nanowires, but cannot fully exclude the parameters that also affect thermoelectric efficiency, i.e. carrier concentration. A systematic quantification of such parameters will be needed to fully exploit the potential of PbTe nanowires for increasing thermoelectric efficiency.

Acknowledgments

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References

[1] Mokari T, Zhang M and Yang P 2007 Shape, size and assembly control of PbTe nanoparticles *J. Am. Chem. Soc.* **129** 9864
[2] Urban J J, Talapin D V, Shevchenko E V and Murray C B 2006 Self-assembly of PbTe quantum dots into nanocrystal superlattices and glassy films *J. Am. Chem. Soc.* **128** 3248
[3] Wang W Z, Poudel B, Wang D Z and Ren Z F 2005 Synthesis of PbTe nanoboxes using a solvothermal technique *Adv. Mater.* **17** 2110
[4] Qiu X F, Loi Y B, Samia A C S, Devadoss A, Burgess J D, Dayal S and Burda C 2005 PbTe nanorods by sonoelectrochemistry *Angew. Chem. Int. Edn* **44** 5855
[5] Tong H, Zhu Y J, Yang L X, Li L and Zhang L 2006 Lead chalcogenide nanotubes synthesized by biomolecule-assisted self-assembly of nanocrystals at room temperature *Angew. Chem. Int. Edn* **45** 7739
[6] Li G R, Yao C Y, Lu X H, Zheng F L, Feng Z P, Yu X L, Su C Y and Tong Y X 2008 Facile and efficient electrochemical synthesis of PbTe dendritic structures *Chem. Mater.* **20** 3306
[7] Fardy M, Hochbaum A I, Goldberger J, Zhang M M and Yang P 2007 Synthesis and thermoelectrical characterization of lead chalcogenide nanowires *Adv. Mater.* **19** 3047
[8] Zhang L, Yu J C, Mo M, Wu L, Kwong K W and Ki Q 2005 A general *in situ* hydrothermal rolling-up formation of one-dimensional, single-crystalline lead telluride nanostructures *Small* **1** 349
[9] Tai G, Zhou B and Guo W 2008 Structural characterization and thermoelectric transport properties of uniform single-crystalline lead telluride nanowires *J. Phys. Chem.* C **112** 11314
[10] Tai G, Guo W and Zhang Z 2008 Hydrothermal synthesis and thermoelectric transport properties of uniform single-crystalline pearl-necklace-shaped PbTe nanowires *Cryst. Growth Des.* **8** 2906
[11] Yan Q, Chen H, Zhou W, Hng H H, Boey F Y C and Ma J 2008 A simple chemical approach for PbTe nanowires with enhanced thermoelectric properties *Chem. Mater.* **20** 6298
[12] Yang Y, Kung S C, Taggart D K, Xiang C, Yang F, Brown M A, Güell A G, Kruse T J, Hemminger J C and Penner R M 2008 Synthesis of PbTe nanowire arrays using lithographically patterned nanowire electrodeposition *Nano Lett.* **8** 2447
[13] Liu W, Cai W and Yao L 2007 Electrochemical deposition of well-ordered single-crystal PbTe nanowire arrays *Chem. Lett.* **36** 1362
[14] Majumdar A 2004 Thermoelectricity in semiconductor nanostructures *Science* **303** 777
[15] Chen G, Dresselhaus M S, Dresselhaus G, Fleurial J P and Caillat T 2003 Recent developments in thermoelectric materials *Int. Mater. Rev.* **48** 45
[16] Wang R Y, Feser J P, Lee J S, Talapin D V, Segalman R and Majumdar A 2008 Enhanced thermopower in PbSe nanocrystal quantum dot superlattices *Nano Lett.* **8** 2283
[17] Beyer H, Nurnus J, Böttner H, Lambrecht A, Roch T and Bauer G 2002 PbTe based superlattice structures with high thermoelectric efficiency *Appl. Phys. Lett.* **80** 1216
[18] Hicks L D, Harman T C, Sun X and Dresselhaus M S 1996 Experimental study of the effect of quantum-well structures on the thermoelectric figure of merit *Phys. Rev.* B **53** R10493
[19] Hicks L D and Dresselhaus M S 1993 Effect of quantum-well structures on the thermoelectric figure of merit *Phys. Rev.* B **47** 12727
[20] Dresselhaus M S, Dresselhaus G, Sun X, Zhang Z, Cronin S B, Koga T, Ying J Y and Chen G 1999 The promise of low-dimensional thermoelectric materials *Microscale Thermophys. Eng.* **3** 89
[21] Lin Y M and Dresselhaus M S 2003 Thermoelectric properties of superlattice nanowires *Phys. Rev.* B **68** 075304
[22] Boukai A, Bunimovich Y, Jamil T, Yu J, Goddard W A III and Heath J R 2008 Silicon nanowires as efficient thermoelectric materials *Nature* **451** 168
[23] Hochbaum A I, Chen R, Delgado R D, Liang W, Garnett E C, Najarian M, Majumdar A and Yang P 2008 Enhanced thermoelectric performance of rough silicon nanowires *Nature* **451** 163
[24] Jang S Y, Lee S H, Kim H S, Roh J W, Jung M K, Kim J H, Lee W Y and Park J H 2008 Transport properties of single-crystalline n-type semiconducting PbTe nanowires *Nanotechnology* **20** 415204
[25] Li D, Wu Y, Kim P, Shi L, Yang P and Majumdar A 2003 Thermal conductivity of individual silicon nanowires *Appl. Phys. Lett.* **83** 2934
[26] Shi L, Li D, Yu C, Jang W, Kim D, Yao Z, Kim P and Majumdar A 2003 Measuring thermal and thermoelectric properties of one-dimensional nanostructures using a microfabricated device *Trans. ASME, J. Heat Transfer* **125** 881
[27] Duke C B, Lazarides A, Paton A and Kahn A 1995 Surface relaxation of PbTe(100) *J. Vac. Sci. Technol.* A **13** 1378
[28] Roh J W, Jang S Y, Kang J H, Lee S H, Noh J S, Kim W C, Park J H and Lee W Y 2010 Size-dependent thermal

conductivity of individual single-crystalline PbTe nanowires *Appl. Phys. Lett.* **96** 103101
[29] Koh Y K, Vineis C J, Calawa S D, Walsh M P and Cahill D G 2009 Lattice thermal conductivity of nanostructured thermoelectric materials based on PbTe *Appl. Phys. Lett.* **94** 153101
[30] Zuev Y M, Lee J S, Galloy C, Park H and Kim P 2010 Diameter dependence of the transport properties of antimony telluride nanowires *Nano Lett.* **10** 3037
[31] Shim W Y, Kim D H, Lee K I, Jeon K J, Ham J H, Chang J Y, Han S H, Jeung W Y, Johnson M and Lee W Y 2008 Magnetotransport properties of an individual single-crystalline Bi nanowire grown by a stress induced method *J. Appl. Phys.* **104** 073715
[32] Shim W Y, Ham J H, Lee K I, Jeung W Y, Johnson M and Lee W Y 2009 On-film formation of Bi nanowires with extraordinary electron mobility *Nano Lett.* **9** 18
[33] Ham J H, Shim W Y, Kim D H, Lee S H, Roh J W, Sohn S W, Oh K H, Voorhees P W and Lee W Y 2009 Direct growth of compound semiconductor nanowires by on-film formation of nanowires: bismuth telluride *Nano Lett.* **9** 2867
[34] Shim W Y, Ham J H, Kim J M and Lee W Y 2009 Shubnikov–de Haas oscillations in an individual single-crystalline bismuth nanowire grown by on-film formation of nanowires *Appl. Phys. Lett.* **95** 232107
[35] Heremans J P, Thrush C M and Morelli D T 2005 Thermopower enhancement in PbTe with Pb precipitates *J. Appl. Phys.* **98** 063703
[36] Boukai A, Xu K and Heath J R 2006 Size-dependent transport and thermoelectric properties of individual polycrystalline bismuth nanowires *Adv. Mater.* **18** 864
[37] Harman T C, Taylor P J, Spears D L and Walsh M P 2000 Thermoelectric quantum-dot superlattices with high ZT *J. Electron. Mater.* **29** L1