APPLIED PHYSICS LETTERS **96**, 103101 (2010)

Size-dependent thermal conductivity of individual single-crystalline PbTe nanowires

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(Received 28 December 2009; accepted 12 February 2010; published online 8 March 2010)

We investigated the thermal conductivity of individual single-crystalline PbTe nanowires grown by a chemical vapor transport method. Thermal conductivities of PbTe nanowires 182–436 nm in diameter were measured using suspended microdevices. The thermal conductivity of a PbTe nanowire appeared to decrease with decreasing nanowire diameter and was measured to be 1.29 W/mK for a 182 nm nanowire at 300 K, which is about half of that of bulk PbTe. Our results indicate that phonon transport through a PbTe nanowire is effectively suppressed by the enhanced phonon boundary scattering due to size effects. © *2010 American Institute of Physics.* [doi:10.1063/1.3352049]

Ever since the discovery of thermoelectricity, it has been challenging to enhance the thermoelectric efficiency of materials, which is characterized by the dimensionless figure-of-merit ZT ($ZT = S^2\sigma T/\kappa$), because S (Seebeck coefficient), σ (electrical conductivity), and κ (thermal conductivity) are interdependent for bulk materials. With the development of nanotechnology, ZT values of nanostructured materials were theoretically predicted to be enhanced by phonon scattering and electron confinement effects, providing opportunities to control S, σ, and κ independently.[1,2] Encouraged by this theoretical prediction, there have been numerous studies to increase ZT using various nanostructured materials over the past decade.[3–9]

In particular, PbTe nanowires have been suggested as promising thermoelectric materials due to the high ZT of bulk PbTe in the mid-temperature range (500–900 K). There have been some studies on the thermoelectric properties of PbTe-based nanostructures such as PbSeTe/PbTe quantum dot superlattices[9] and PbTe with nanosized grain structure.[10] Even so, there has been no systematic study on the diameter-dependence of thermal conductivity of individual single-crystal PbTe nanowires, which is of critical importance in predicting the phonon mean free path, although Yang and co-workers[11] have investigated the thermal conductance of PbTe nanowires. For this reason, in this paper, we report the effect of nanowire diameter on thermal conductivity of individual single-crystalline PbTe nanowires grown by a chemical vapor transport (CVT) method.

In order to grow single-crystalline PbTe nanowires using the CVT method, two kinds of source materials, i.e., lead (II) chloride ($PbCl_2$, 99.999%) and tellurium (Te, 99.8%) powders were evaporated at 1100 °C for 2 h under an Ar flow of 300 SCCM inside a quartz tube reactor. The evaporated Pb and Te reacted with Au catalytic nanoparticles on a thermally oxidized Si (100) substrate, forming a liquid alloy of PbTe. The liquid alloy was subsequently solidified at the interface of liquid and solid following the vapor-liquid-solid mechanism. As shown in Fig. 1(a), it was found that uniform and straight PbTe nanowires with high aspect ratio are grown on

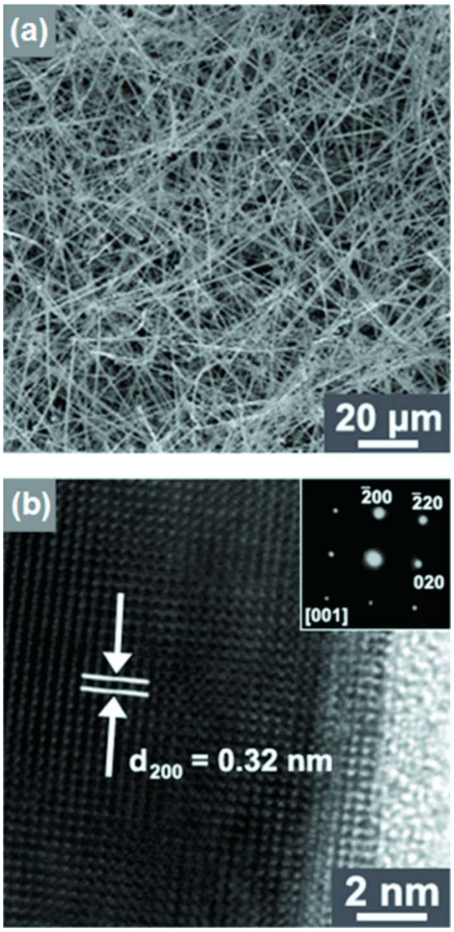

FIG. 1. (Color online) (a) A SEM image of PbTe nanowires grown by the CVT method. (b) A high-resolution TEM image of a single-crystalline PbTe nanowire. The inset shows a SAED pattern for this PbTe nanowire.

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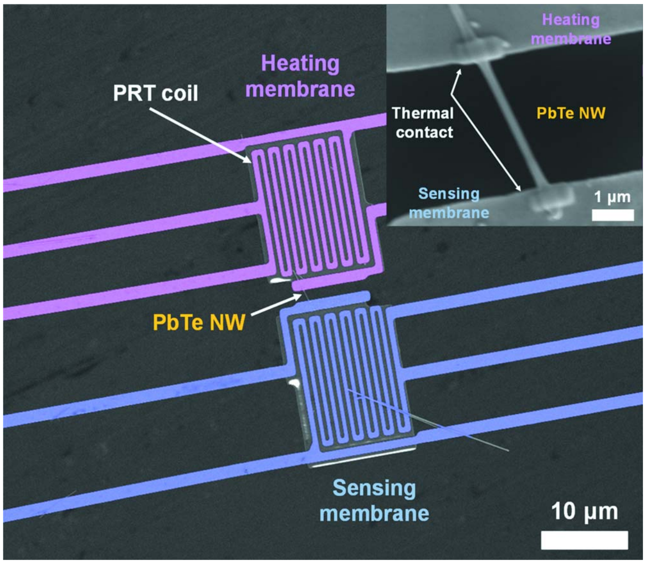

FIG. 2. (Color online) A SEM image of an individual PbTe nanowire placed on the suspended microdevice. Pt/C thermal contact was deposited locally using a dual-beam FIB to prevent thermal resistance build-up between the PbTe nanowire and membranes (inset).

the Si substrate after heat treatment. A high-resolution transmission electron microscopy image and a corresponding selected area electron diffraction (SAED) pattern demonstrate that the PbTe nanowires are high quality single-crystalline with a growth direction of [100], as shown in Fig. 1(b). PbTe nanowires grown by the CVT method are a single PbTe phase with a ratio Pb/Te≈1, based on our previous high-resolution x-ray diffraction and energy-dispersive x-ray fluorescence spectroscopy studies.[12]

Suspended microdevices were employed to measure the thermal conductivity of individual PbTe nanowires without thermal conduction through the substrate.[3,7,13] Figure 2 shows a scanning electron microscopy (SEM) image of a suspended microdevice that consists of two adjacent silicon nitride ($\mathrm{SiN_x}$) membranes, which are suspended with five long $\mathrm{SiN_x}$ beams. A Pt resistance thermometer (PRT) coil with a width of 1 μm and a thickness of 30 nm, which acts as both a heater to increase the temperature of a membrane and a thermometer to measure the temperature of the membrane, was patterned on each membrane. An individual PbTe nanowire was placed between the two membranes by use of drop-casting (see Fig. 2). Then, in order to reduce the thermal contact resistance between the PbTe nanowire and each membrane, Pt/C thermal contacts on each membrane were locally deposited using a dual-beam focused ion beam (FIB), as shown in the inset of Fig. 2. Taking advantage of suspended microdevices and the Pt/C thermal contact, the PbTe nanowire should be the only pathway to transport heat between the heating membrane and the sensing membrane.

The thermal conductivity of PbTe nanowires was measured in the temperature range of 40–300 K, using a closed cycle cryostat. All measurements were carried out in a high vacuum of less than 5×10^{-6} Torr in order to eliminate convectional heat loss. Details about the thermal conductivity measurement and analysis using the suspended microdevices were provided previously in other papers.[13] Direct current voltage was applied to the PRT coil on the heating membrane, resulting in Joule heat generation and a consequent temperature increase (T_h). A certain amount of heat generated by the PRT coil on the heating membrane is transported to the sensing membrane through an individual PbTe nanowire with negligible heat loss. Heat conduction via the PbTe nanowire allows the temperature of the sensing membrane (T_s) to also increase. The temperature difference between heating and sensing membranes was controlled within 5 K to prevent radiation of heat. Under thermal steady state conditions, the thermal conductivity through a PbTe nanowire is calculated from thermal conductance, which is derived from T_h, T_s, and a measured temperature coefficient of resistance of each PRT coil.

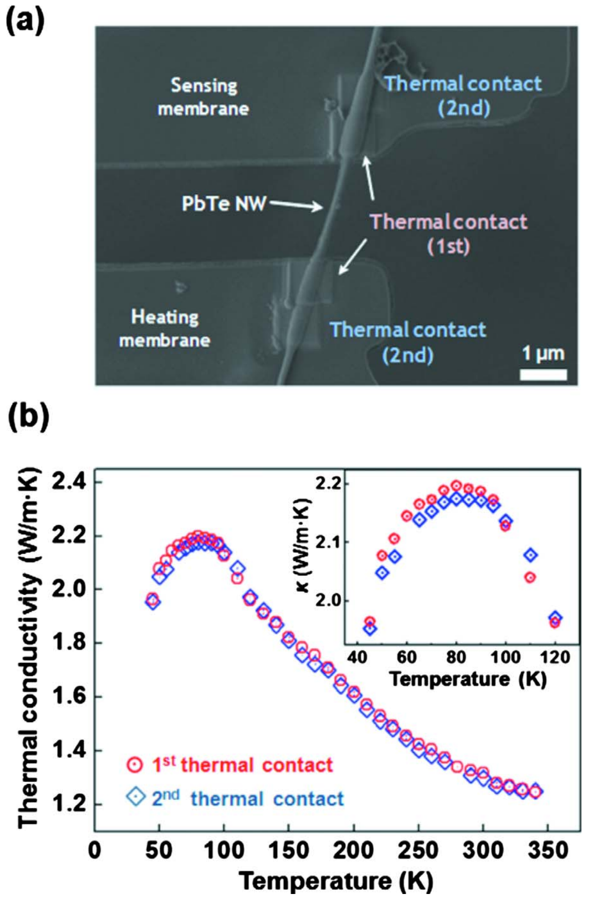

FIG. 3. (Color online) (a) A SEM image of an individual PbTe nanowire on the membranes after formation of the second thermal contacts. (b) Measured thermal conductivities for a PbTe nanowire with $d=182$ nm before and after formation of the second thermal contacts. The maximum difference in thermal conductivities was 0.4 W/mK at 110 K (inset).

The effect of the thermal contact on the thermal conductivity measurement was confirmed by making the Pt/C contact twice and comparing its thermal conductivity with the single contact case. The second thermal contact was similar to the previous one in size and therefore the total area doubled, as shown in Fig. 3(a). Figure 3(b) shows the measured thermal conductivities for a PbTe nanowire with a diameter (d) of 182 nm in the temperature range of 40–340 K before and after the fabrication of the second thermal contact. As shown, there is almost no change in thermal conductivity of the 182 nm nanowire after the formation of the additional thermal contact. The maximum difference of thermal conductivities was less than 0.04 W/mK in the temperature range of 40–340 K, representing the maximum ratio of thermal conductivities difference was less than 1.4%. This

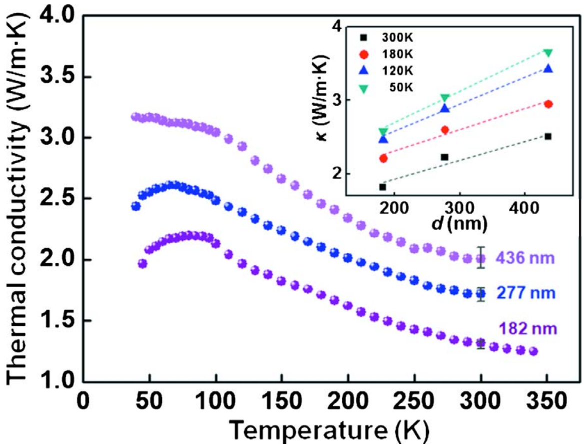

FIG. 4. (Color online) The measured thermal conductivities of individual single-crystalline PbTe nanowires with $d=182$, 277, and 436 nm. The inset shows the diameter dependencies of thermal conductivity at temperatures of 50, 120, 180, and 300 K.

result indicates that the thermal contact resistance of the Pt/C thermal contact is negligible.

Figure 4 shows the thermal conductivity of individual PbTe nanowires with $d=182$, 277, and 436 nm in the temperature range of 40–300 K. The thermal conductivity of a PbTe nanowire with $d=182$ nm was measured to be 1.29 W/mK at room temperature, which is half of the value of bulk PbTe ($\kappa \approx 2.4$ W/mK at 300 K).[14] Based on the thermal conductivity of individual PbTe nanowires with various diameters, as shown in Fig. 4, the thermal conductivity of a nanowire decreases as its diameter shrinks. Considering that phonon boundary scattering has a considerable effect in reducing the thermal conductivity of a nanowire, this result clearly suggests that the enhanced boundary scattering caused by the size effect suppresses phonon transport through the PbTe nanowires.[3,15] The thermal conductivity of a PbTe nanowire with $d=436$ nm at 300 K have a similar value to that of bulk PbTe, but that of the PbTe nanowire with $d=277$ nm is less than that of bulk PbTe. From this, the phonon mean free path in PbTe at 300 K was estimated to be somewhere between 277 and 436 nm.[3,16]

As shown in Fig. 4, the thermal conductivity of individual PbTe nanowires increases with decreasing temperature until it reaches their maximum, resembling the temperature dependence of bulk single-crystalline PbTe. Thermal conductivity peaks appear around 80 and 70 K for the respective PbTe nanowire with $d=182$ and 277 nm, while bulk PbTe exhibits its peak at ~10 K.[17] This also indicates that there is a strong phonon boundary scattering, because it has been shown previously in Si nanowires that maximum peak of thermal conductivity shifted to the higher temperature when there exists strong phonon boundary scattering.[3] For a PbTe nanowire with $d=436$ nm, the peak would presumably occur below the lower temperature limit of our experiments (40 K). This size-dependent peak shift indicates phonon boundary scattering becomes dominant over phonon-phonon Umklapp scattering as the nanowire diameter grows smaller. The inset of Fig. 4 shows this diameter dependence of thermal conductivity and the influence of temperature more clearly. The slope of the κ versus d plot becomes steeper as the temperature is reduced. From this trend, it is inferred that the phonon boundary scattering due to the size effect is greatly enhanced at a lower temperature, hence the low temperature phonon transport is more effectively suppressed by the reduction in nanowire diameter. These results are in good agreement with the general temperature dependence of thermal conductivity, in which the long wavelength phonons, which carry most of heat at lower temperatures, are predominantly scattered by crystal boundaries.

In summary, the thermal conductivities of individual single-crystalline PbTe nanowires with $d=182$, 277, and 436 nm, which were grown by a chemical vapor transport method, were measured using suspended microdevices. The thermal conductivity decreases as the nanowire diameter shrinks, indicating that phonon transport through a PbTe nanowire is suppressed due to the strong phonon boundary scattering in the one-dimensional structure. The phonon boundary scattering in PbTe nanowires was found to be more dominant at lower temperatures since the nanowire surface is a major scattering source for the long wavelength phonon. Our results suggest that PbTe nanowires grown by the vapor transport method can be applied for future high-efficiency thermoelectric devices.

This work was supported by Priority Research Centers Program (Grant No. 2009-0093823), Basic Science Research Program through the National Research Foundation of Korea (NRF), by a grant from "Center for Nanostructured Materials Technology" under "21st Century Frontier R&D Programs" of the Ministry of Education, Science and Technology, and by Seoul R&BD Program (10816). J.P. is grateful for the financial support of a grant from the WCU (World Class University) program (R31-10035). J.W.R. thanks the financial support of the Seoul Science Fellowship. We thank Professor A. Majumdar and K. Hippalgaonkar at the University of California, Berkeley and Professor R. Chen at the University of California, San Diego for helpful discussions and assistance with thermal characterization. J.W.R. and S.Y.J. equally contributed to this work.

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