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MEASUREMENTS OF THERMOELECTRIC PROPERTIES OF BISMUTH TELLURIDE NANOWIRES

Jianhua Zhou, Li Shi[1, 2]
[1]Department of Mechanical Engineering, [2]Center for Nano and Molecular Science and Technology, University of Texas at Austin, Austin, TX 78712

Chuangui Jin, Xiaoguang Li[3]
[3]Hefei National Laboratory for Physical Science at Microscale, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

ABSTRACT

Theoretical calculations have predicted that nanowire materials may have enhanced thermoelectric figure of merit compared to their bulk counterparts due to classical and quantum size effects. We have measured the thermoelectric properties of bismuth telluride nanowires deposited using an electrochemical deposition method in porous anodized alumina templates with the average pore size of about 60 nm. Transmission electron microscopy results of these nanowires showed that the nanowires were single crystalline with a composition of 54% Te and 46% Bi and the thickness of the surface oxide layer was in the range of 5-10 nm. The thermal conductance and Seebeck coefficient of the nanowires were measured using a microfabricated device that consists of two suspended membranes, across which the nanowire sample was placed. The obtained Seebeck coefficient of a bundle consisting of two 100 nm bismuth telluride nanowires increased with increasing temperature from 160 K to 360 K, and the room temperature value was 260 μV/K, which was 60% higher than the bulk value. The thermal conductance of the sample also increased with increasing temperature from 25 K to 360 K. Current design of the microdevice does not allow for four-probe electrical resistance measurement of the nanowire. We have measured the four-probe electrical resistance of a 57 nm diameter and a 43 nm diameter bismuth telluride nanowires from the same template, and found that the room-temperature electrical conductivity of the nanowires was close to the bulk value and showed much weaker temperature dependence than bulk electrical conductivity.

INTRODUCTION

In order to obtain a coefficient of performance comparable to those of vapor compression refrigeration units based on chlorofluorocarbon(CFC), the thermoelectric figure of merit (*ZT*) of Peltier refrigerators needs to be higher than 3 [1]. *ZT* is defined as $ZT = S^2\sigma T/\kappa$ [2], where *S* is the Seebeck coefficient, *σ* is the electrical conductivity, *κ* is the thermal conductivity, and *T* is the temperature. For bulk materials the improvement of *ZT* has been limited because the three properties are coupled with each other. Improving one of the three materials properties often has negative effects on one of the other two. The best bulk materials for thermoelectric cooling have been bismuth telluride alloys such as $Bi_{0.5}Sb_{1.5}Te_3$, with $ZT \approx 1.0$ at 300K [2]. Low dimensional materials including nanowires provide new approaches to improving the *ZT*. When the diameter of the nanowires becomes comparable to the electron wavelength, quantum confinement of charge carriers can lead to a large electron density of states near the Fermi level and an improvement in the power factor ($S^2\sigma$) [3]. In addition, the thermal conductivity can be suppressed due to increased boundary scattering of phonons and other phonon confinement effects [4]. One of the early theoretical calculations showed that the *ZT* value of a single-crystal Bi_2Te_3 nanowire of square cross section and width 0.5 nm could be as high as 14 [5]; while recent calculations suggest that Bi-based [6] and III-V [7] nanowires with more realistic diameters on the order of 10 nm can have a ZT value as high as 6.

In the past decade, several synthesis techniques have been developed to grow Bi_2Te_3 nanowires. For example, a pulsed laser ablation method was used to synthesize single crystalline Bi_2Te_3 nanowires [8], while electrochemical deposition of bismuth and tellurium into nanopores of anodic alumina templates successfully produced polycrystalline [9] and single crystalline [10] Bi_2Te_3 nanowires. Although there have been intense efforts to characterize these nanowires, little progress has been made to verify the improvement of thermoelectric figure of merit in Bi_2Te_3 nanowires [11, 12].

In the present work, we used a suspended micro-fabricated device to measure the thermal conductivity and Seebeck coefficient of individual single-crystal bismuth telluride nanowires grown by the electrochemical deposition method. In addition, the four-probe electrical resistance of different nanowires from the same template was measured separately. In the measurements, a Pt layer was deposited on the contacts to the nanowire using Focused Ion Beam (FIB) deposition to improve the thermal and electrical contacts [11, 13]. The experimental results showed that the thermal conductance increased with increasing temperature from 25 K to 360 K; the Seebeck coefficient was 260 μV/K at room temperature, which was 60% higher than the bulk value, and increased with increasing temperature from 160 K to 360 K; the electrical conductivity was close to the bulk value and increased with increasing temperature from 4.2 K to 390 K.

EXPERIMENTAL METHODS

Bismuth telluride nanowires were grown in an anodic alumina membrane (AAM) by using an electrochemical deposition method [10]. The growth direction of the nanowire is along the <110> direction, perpendicular to the c-axis. The average pore size of the AAM was about 60 nm. After the AAM was dissolved in a NaOH solution, the residue was rinsed with de-ionized water and the nanowires were dispersed in ethanol. The high resolution transmission electron microscope (HRTEM) images of the nanowires in Fig. 1 revealed that these nanowires were single crystalline with a 5-10 nm thick surface oxidation layer. An energy dispersive spectrometer (EDS) analysis showed that the chemical composition of the nanowires was 54% tellurium (Te) and 46% bismuth (Bi).

For thermal conductivity and Seebeck coefficient measurements, the nanowire was assembled onto a suspended micro-device by a fluid alignment method. Figure 2 shows a scanning electron microscope (SEM) image of a micro-device. The detailed description of these devices can be found in references 11, 13 and 14. In brief, the micro-device consisted of two adjacent symmetric silicon nitride (SiN_x) membranes. Each membrane was suspended by five long SiNx beams and contains a serpentine platinum (Pt) line and a Pt electrode. The serpentine Pt line was used as an electrical heater and a platinum resistance thermometer (PRT).

After a nanowire was trapped between the two membranes, a 200 nm-thick layer of Pt was deposited using FIB on the two contacts of the nanowire to improve the electrical and thermal contacts. After the micro-device was packaged and wire bonded, it was placed in an evacuated liquid helium cryostat (Janis ST-475) with a temperature range from 4.2 K to 400 K. During the experiment, a DC current was supplied to one of the two PRTs to raise the temperature of the corresponding membrane (heating membrane) by Joule heating. Heat conduction through the nanowire caused an increase in the temperature of the other membrane (sensing membrane). We measured the temperature rises of the two membranes using an AC differential resistance measurement method after obtaining the temperature coefficient of resistance (TCR) of each PRT. We found that heat conduction through the nanowire was several orders of magnitude larger than parasitic heat transfer between the two membranes through the residual gases in the evacuated cryostat and by radiation. The thermal conductance of the nanowire was obtained following the procedure in reference 14. In addition, we measured the thermoelectric voltage across the nanowire using the two electrodes at the edges of the two membranes so as to obtain the Seebeck coefficient of the nanowire.

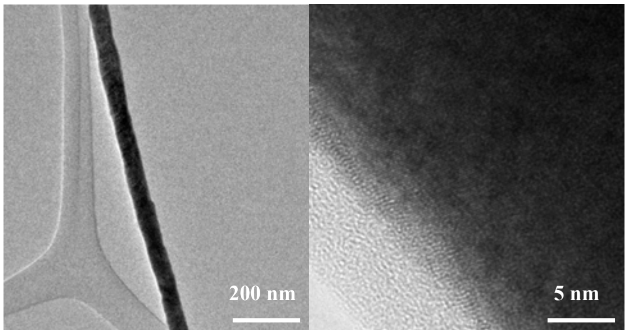

Figure 1. HRTEM images of a bismuth telluride nanowire with a diameter of 57 nm. The left image shows that the nanowire has a high aspect ratio and the right image shows that the wire is single crystal with a 8 nm thick oxide layer.

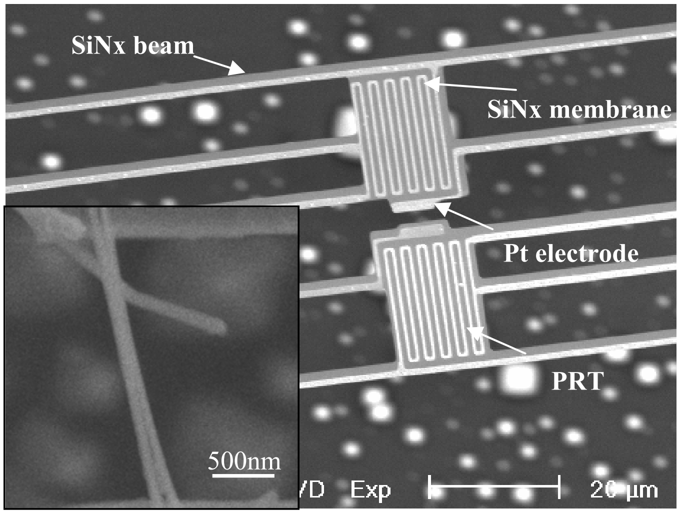

Figure 2. A SEM image of a micro-device. The inset shows that two individual bismuth telluride nanowires, each with a diameter of 100nm, bridge the two membranes.

One of the deficiencies of the current design of the micro-device is that there is only one Pt electrode on each membrane, so that it can not be used to measure the four-probe electrical resistance. The four-probe resistance and the electrical conductivity of different nanowires from the same AAM were measured separately using a different method. In this method, four 200 μm by 200 μm metal contact pads were patterned using Electron Beam Lithography (EBL) on a 1 μm thick SiO_2 film grown on a silicon wafer. After a drop of the nanowire solution was dispersed and dried on the wafer, we employed FIB to deposit four small Pt electrodes to connect the nanowire and the large metal contacts. The four-probe electrical resistance of the nanowire was measured as a function of temperature in the cryostat.

MEASUREMENT RESULTS AND DISCUSSION

The thermal conductance and Seebeck coefficient of a nanowire bundle consisting of two nanowires (Fig. 2) were measured using the microdevice. The diameter of each nanowire was about 100 nm. To improve the electrical and thermal contacts, a 200 nm thick Pt layers were deposited on the contacts to the nanowires by using FIB deposition. Effects of thermal contact resistance on the measurement results and the measurement uncertainties were discussed in references 14 and 16.

Thermal Conductance

Figure 3 shows that the measured thermal conductance of the nanowire bundle increased as a function of temperature from 25 K to 360 K. This trend differs from that of bulk Bi_2Te_3, for which the thermal conductivity peaks at a temperature below 75K, decreases with increasing temperature to a minimum at about 270 K, and shows a sharp upturn above 270 K [17]. The sharp upturn was believed to arise largely from the transport of the gap energy by ambipolar diffusion. Also, the electron and phonon contributions to the thermal conductivity of bulk Bi_2Te_3 are comparable to each other. For the nanowire, the absence of a thermal conductivity maximum below 390 K suggests that boundary scattering plays a dominant role in phonon and charge transport in this temperature range. Due to heat leakage through a short nanowire segment contacting the two nanowires (inset to Fig. 2), we were not able to obtain the accurate thermal conductivity of the two nanowires.

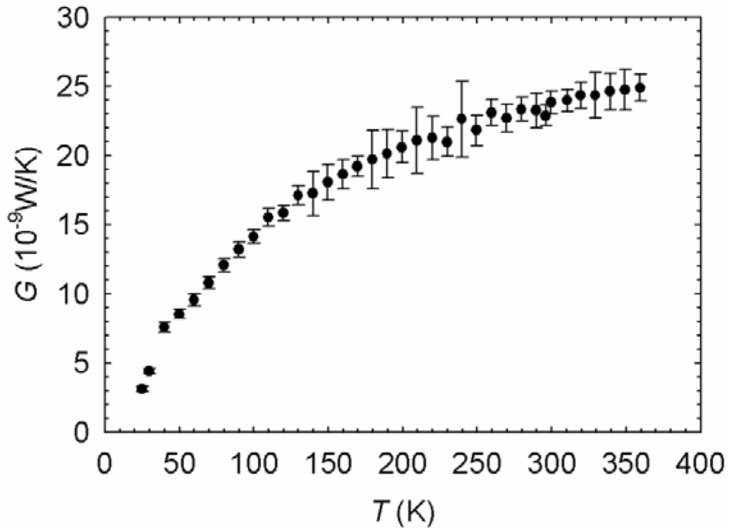

Figure 3. Thermal conductance of the bismuth telluride nanowires in the temperature range of 25 K to 360 K.

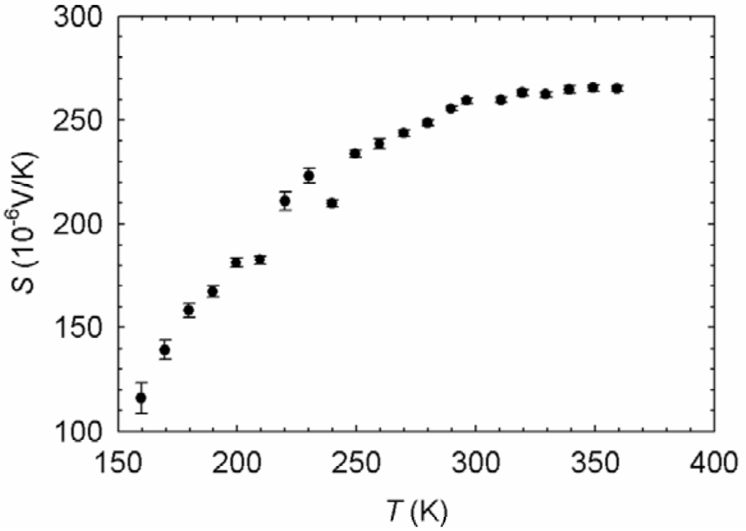

Figure 4. Seebeck coefficient of the nanowires in the temperature range of 160 K to 360 K.

Seebeck Coefficient

An electrometer with input impedance larger than 10^{15} Ω was used to measure the thermoelectric voltage across the nanowires. With the deposition of a Pt layer on the two contacts using FIB, the two-probe resistance of the nanowires was 1.5 MΩ at room temperature and increased exponentially up to about 80 MΩ when the temperature decreased to 160 K. The high resistance at low temperatures led to an increase in noise in the measured thermoelectric voltage across the nanowires. The obtained Seebeck coefficient of the two nanowires is shown in Fig. 4. The Seebeck coefficient increased with increasing temperature from 160 K to 360 K, somewhat similar to the trend for the optimally doped bulk bismuth telluride [11]. At room temperature, the measured Seebeck coefficient was 260 µV/K, about 60% higher than the value for bulk $Bi_{0.46}Te_{0.54}$ crystals [18]. The origin of this high Seebeck coefficient in the nanowire is intriguing. Because of the large diameter, it is questionable whether the high Seebeck coefficient was due to quantum confinement.

Electrical Conductivity

We have measured the four-probe resistance of two individual bismuth telluride nanowires. Figure 5 shows a SEM image of a nanowire contacted by four FIB-patterned electrodes. The diameter of the wire was measured to be about 57 nm by using an Atomic Force Microscope (AFM). The length between the two middle electrodes was 6 µm. An electrometer was used to measure the voltage drop across the two middle electrodes when a dc current was supplied to the nanowire between the two outer electrodes, where Peltier cooling or heating took place. The separation between the two outer electrodes and the adjacent middle electrodes was larger than 3 µm. Further, the current used in the measurement was very small (0.1 – 1 µA maximum) and the nanowire was in contact with the substrate. Consequently, the temperature difference associated with the Peltier effects between the two middle electrodes was estimated to be very small so that the thermoelectric voltage drop across the two middle electrodes can be neglected. As shown in figure 6, the room temperature electrical conductivity value of 0.17 $(\mu m \cdot \Omega)^{-1}$ was about 10% lower than the bulk value of 0.19 $(\mu m \cdot \Omega)^{-1}$ [18]. In addition, the measured electrical conductivity decreased slightly with decreasing temperature from 380 K to 25 K and changed very slowly from 25 K to 4.2 K. The observed temperature dependence was much weaker than that for bulk bismuth telluride crystal, for which the electrical conductivity decreases rather rapidly with increasing temperature due to increased electron-phonon scattering. Although the weaker temperature dependence for the nanowire could be attributed to increased boundary scattering of electrons, the high conductivity at room temperature suggests that surface scattering did not cause an apparent reduction in the electrical conductivity at room temperature. Another possible cause for the weak temperature dependence is a slightly larger band-gap of the nanowire than the bulk value. The existence of a larger band-gap can cause a

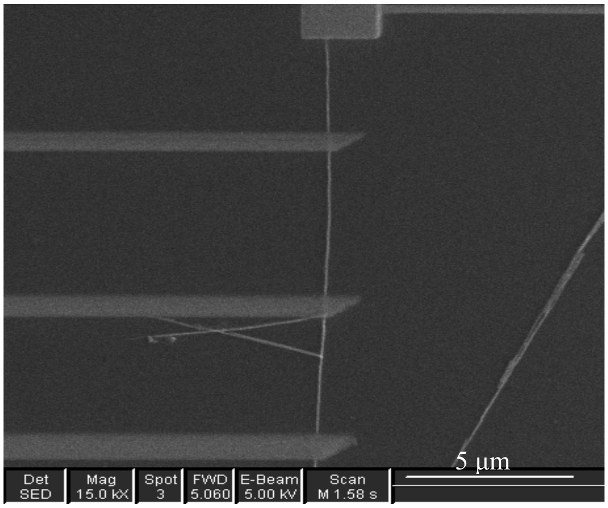

Figure 5. A SEM image of a bismuth telluride nanowire that was used for measuring the four-probe electrical resistance.

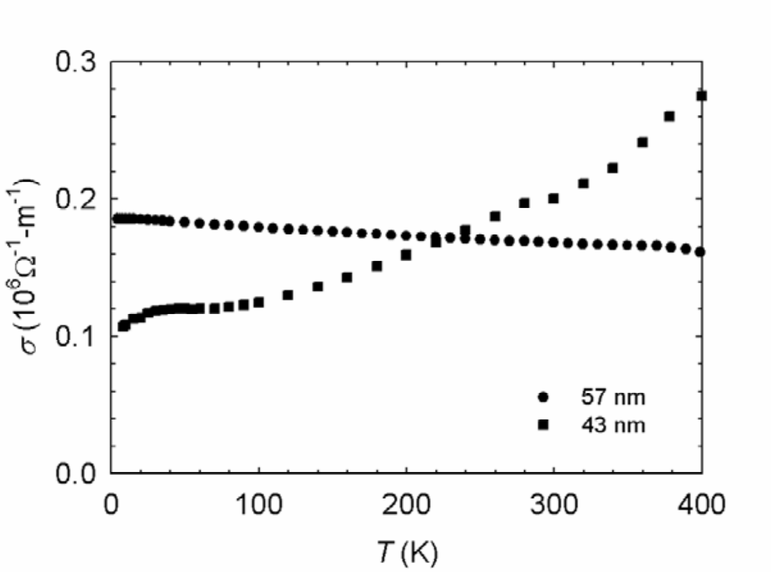

Figure 6. Electrical conductivity of bismuth telluride nanowires with diameters of 57 nm and 43 nm

more rapidly decrease in the carrier density at low temperatures. The latter effect could compete with the effect of temperature on the carrier mean free path, and cause a weaker dependence of the electrical conductivity on temperature. If the band-gap is increased further, the effect on the carrier density could become more important than that on the carrier mean free path, and causing an increase of conductivity with increasing temperature. In fact, such trend was observed for another smaller (43 nm diameter) nanowires, as shown in Fig. 6. A recent study using scanning tunneling spectroscopy (STS) also revealed that the band-gap of silicon nanowires increased with decreasing diameter [19], and there have been theoretical reports of an increased band-gap of BiSb nanowires [20] with a decreased nanowire diameter. However, this behavior has not been reported for Bi_xTe_{1-x} nanowires and requires further studies.

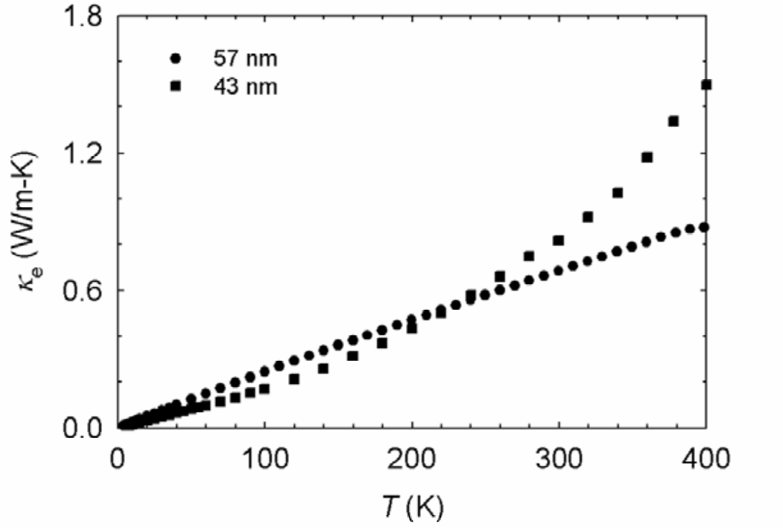

Figure 7. Electronic thermal conductivity of bismuth telluride nanowires with diameters of 57 nm and 43 nm

Because the measured electrical conductivity of bismuth telluride nanowires was only one or two orders of magnitude lower than metals, the electron contribution to the thermal conductivity could not be neglected. Using the same Lorentz number L = 1.36×10^{-8} W-Ω/K^2 as for bulk bismuth telluride with $\sigma = 0.17$ (Ω·µm)$^{-1}$ [21], we have calculated κ_e using the Wiedemann-Franz law. The result is shown in Fig. 7.

CONCLUSION

We have measured the temperature-dependant thermal conductance, Seebeck coefficient, and electrical conductivity, of single-crystal bismuth telluride nanowires synthesized using an electrochemical deposition method. At room-temperature, the obtained Seebeck coefficient of a bundle consisting of two 100 nm diameter nanowires were about 60% higher than the bulk value, while the thermal conductance of the bundle increased with increasing temperature in the temperature range of 25 K to 360 K. The electrical conductivity of a 57 nm diameter and a 43 nm diameter nanowire was very close to the bulk value.

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