Thermoelectric power of single crystalline lead telluride nanowire

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Abstract. In this study, structurally uniform PbTe nanowires (NWs) with high-quality single crystals were synthesized using a stress-induced growth. Selected-area electron diffraction patterns show that the PbTe NWs were grew along the [100] direction. The thermoelectric power \( S \) of a 142-nm diameter NW plotted for temperature range of 300–350 K exhibited semiconductor \( n \)-type behavior. The absolute \( S \) plotted against carrier concentration \( n \) was size-dependent, compared with our previous work.

1. Introduction
Nanowires (NWs) used for converting waste heat into electricity have become an attractive research topic [1–5]. In general, Thermoelectric can be utilized for power generation and cooling applications [6–11]. PbTe is a semiconductor with an energy band gap of 0.32 eV at 300 K, it is suitable for application in thermoelectricity [10,12–14]. The efficiency of thermoelectric materials is determined according to the dimensionless figure of merit \( ZT \), which is defined as \( S^2\sigma T/(\kappa_e + \kappa_l) \), where \( S \) is the thermoelectric power (or Seebeck coefficient), \( \sigma \) represents the electrical conductivity, \( \kappa_e \) is the electronic thermal conductivity, and \( \kappa_l \) is the lattice thermal conductivity. Numerous studies have reported that nanomaterials enhance the \( ZT \) as a result of quantum confinement effects and increased surface phonon scattering [11,15–16]. In NWs comprising thermoelectric materials such as PbTe, the nanometer scale is predicted to increase the value of \( S \) [17–18]. Furthermore, previous studies on the thermoelectric properties of PbTe NWs have reported inconsistent findings, primarily because fabricating electrical Ohmic contacts for PbTe NWs remains extremely difficult. Specifically, the native oxide layer that forms on the outer surface of PbTe NWs can be removed only by using a focus ion beam (FIB). In this study, we report how nanowire diameter influences the electronic contribution to the thermoelectric transport properties in single-crystal PbTe NWs.

2. Experiment Design
PbTe NWs were synthesized using stress-induced growth described in reference [19–20], which is a practical method for growing NWs with a high aspect ratio and high crystallinity. As-received Pb (Alfa Aesar, -200 mesh, 99.9%) and Te (Alfa Aesar, -325 mesh) powders were first mixed at a specific ratio and melted at 1000 °C for 4 h in a vacuumed quartz tube below \( 5 \times 10^{-6} \) Torr. The molten compound was slowly cooled to room temperature in the furnace. Subsequently, the compound was cut to form a disk, which served as the target for the pulsed laser deposition. Single-crystal SiO\(_2\)/Si (100) wafers (e-light Tech. Inc.; SiO\(_2\) thickness, 413–434 nm; diameter, 100 ± 0.5 mm) with double-side polishing were cut into squares measuring approximately 1.5 cm\(^2\). All substrates were cleaned
using acetone, isopropyl alcohol, and deionized water in an ultrasonic bath for 10 min before being dried with N\textsubscript{2} stream. The PbTe films were prepared in an ArF excimer laser (Lamda Physik LPXpro 210) and deposited onto substrates in a vacuum system with a base pressure of 5.0 × 10\textsuperscript{-7} Torr. The PbTe thin films were grown with deposition rate at 0.22 Å/s, which the excimer laser was applied at 140 mJ (frequency, 10 Hz) for 15 min at room temperature. The substrate was rotated at approximately 10 rpm, and the thickness of the films was 20 nm. The films were sealed in a vacuumed quartz tube below 5 × 10\textsuperscript{-6} Torr, annealed at 450 °C for 5 d, and then left in the furnace to cool to room temperature. During the annealing process, the NWs grew from the film and released compressive stress because of the difference between the thermal expansion coefficient of the PbTe film and that of the SiO\textsubscript{2}/Si substrate.

3. Results and Discussion
Field emission scanning electron microscopy (FESEM; Hitachi, S-4800) images of the PbTe NWs (Fig. 1a) show that the NWs exhibited diameters ranging from 50 to 300 nm, and lengths up to several micrometers. Figure 1b shows a TEM image and the lattice fringes of the smooth PbTe NW that were separated by a 0.33-nm gap were consistent with a periodicity along the [200] direction with the lattice parameter $a$ of approximately 6.549 Å (Fig. 1b) was 1.87% higher than that of the PbTe annealed thin film ($a = 6.43$ Å), possibly as a result of antisite defects (Pb\textsubscript{Te}).

![Figure 1](image.png)

**Figure 1.** (a) SEM image (top view) showing that all of the PbTe NWs grew several micrometers in length from the surface of the PbTe thin film; (b) The distance between the crystal faces is 0.33 nm, indicating that the lattice fringes grew along the [200] direction; the inset of the Fig. 1b shows the SAED pattern (at the [001] zone axis), confirming the single-crystalline NWs grew in the [100] direction; and (c) SEM images of a single-crystal PbTe NW (diameter d, 142 nm; length l, 18.95 µm) placed on a Si\textsubscript{3}N\textsubscript{4} template following electrode formation by using an FIB.
A corresponding selected-area electron diffraction (SAED) pattern show that the PbTe NWs were high-quality single crystals (the inset of Fig. 1b). The chemical composition of the PbTe NWs was examined using energy dispersive X-ray spectroscopy (EDS), and the stoichiometric composition of the individual NW was Pb$_{1.1}$Te$_{0.9}$. A tungsten needle (d = 100 nm) and a binocular optical microscope were used to extract a single-crystal NW from the PbTe thin film, which was then suspended by electrodes on a Si$_3$N$_4$ microchip (Fig. 1c). Subsequently, the microchip was used to obtain the values of S and $\sigma$ (range, 50–350 K) by using four-point measurements (Fig. 1c).

Figure 2a shows the temperature dependence of $\sigma$ and S in 50–350 K for a 142-nm NW that exhibited a semiconducting behavior. The $\sigma$ at near room temperature was 2383 S m$^{-1}$, which was 96% lower than that of the PbTe bulk (65789.47 S m$^{-1}$) [14], which was possibly caused by the surface scattering of charge carriers [19,21]. However, the value was higher than those reported in previous studies [19, 22–24].

Figure 2. Temperature dependence of (a) electrical conductivity $\sigma$ and thermoelectric power S; and (b) thermoelectric power factor for a single-crystal PbTe NW (d = 142 nm).

The S value was -162 $\mu$V K$^{-1}$ for the 142-nm NW at 300 K, which is approximately 7.43% less than that of the PbTe bulk NW (-175 $\mu$V K$^{-1}$) [14], and might have resulted from structural imperfections
such as antisite defects that were caused by the creation of a vacancy at the Te site, thereby facilitating the enhanced carrier concentration $n$ [14,25]. A negative $S$ value indicates that the PbTe NW is an $n$-type semiconductor because the electrons exhibited considerably higher carrier mobility $\mu$ than the holes did, thereby dominating the electrical transport properties and that the $S$ was controlled using electron diffusion [26–27]. The values of $\sigma$ correlated closely with $S$, and the curve of $\sigma$ was inverse with that of $S$ (Fig. 2a); thus, at 300 K, the thermoelectric power factor ($S^2\sigma = 93.50 \mu W m^{-1} K^{-2}$) was greater than those reported in previous studies [22–24,25]. Figure 2b shows the $S^2\sigma$ of the PbTe NW as a function of temperature. The power factor gradually increased in conjunction when the temperature increased, which was primarily attributed to the observed $\sigma$ trends of the PbTe NW. According to the Mott relation [6], the carrier concentration $n$ can be estimated from thermoelectric power data as:

$$S = \frac{8\pi^2k_B^2}{3q\hbar^2}m^*_d T\left(\frac{\pi}{3n}\right)^{2/3}$$  \hspace{1cm} (1)$$

where $k_B$ is Boltzmann’s constant, $m^*_d$ is the effective mass of the carrier ($m^*_d = 0.30 m_o$ in PbTe) [29], $m_o$ is the electron mass, $q$ represents the electron charge, $h$ is Planck’s constant, and $T$ is the temperature. Previous studies have shown that this equation is valid for degenerate semiconductors with an $n$ value ranging from $10^{18}$ to $10^{20}$ cm$^{-3}$ [27,30]. The $n$-value was approximately $3.80–7.14 \times 10^{18}$ cm$^{-3}$ in the $300–350$ K range, indicating that the NW exhibited degenerative semiconductor behavior. The value of $n$ decreased as $T$ increased to $320$ K, and $n$ remained relatively constant over a wide range of temperatures at $320–350$ K [Fig. 3a, marked by the white circles with a black outline], thus indicative of extrinsic doping. The values of $\mu$ were calculated using the equation:

$$\mu = \frac{1}{\rho n q} = \frac{\sigma}{n q}$$  \hspace{1cm} (2)$$

where $n$ is the carrier concentration, $\sigma$ represents the electrical conductivity, and $q$ is the electron charge. The calculated values of $\mu$ ranged from 20.92 to $45.71$ cm$^2$ V$^{-1}$ s$^{-1}$ [Fig. 3a, marked by the white squares with a blue outline], which were considerably lower than those of the PbTe bulk (approximately $209$ cm$^2$ V$^{-1}$ s$^{-1}$) [14], indicating that the carrier mobility of the NW was approximately 90% slower than that of the PbTe bulk at room temperature. The $\mu$ values of the $142$ nm NW exhibited a continuous increase in conjunction with $T$ from room temperature to $330$ K, indicating that the scattering of impurities was dominant throughout the entire temperature range. The effect of ionized impurities in semiconductor on $\mu$ is given by the equation $\mu_i \sim (m^*)^{1/2} N^{1/2}$, where $N$ is the density of the total ionized impurities in the semiconductor [30]; thus, $\mu$ remained relatively flat over a wide range above $330$ K, thereby indicating that electron scattering had occurred throughout the entire NW (i.e., the scattering was caused by defects or impurities). Figure 3b shows the absolute value of the $S$ for the various PbTe samples as a function of the carrier density at room temperature. In bulk PbTe, in which acoustic-phonon scattering dominates, the $S(n,p)$ curve follows the full line shown [14]. The $S$ value of PbTe NW ($d = 142$ nm) exist on the full line. The values of $S$ correlated closely with those of $n$, which was consistent with the samples where a low $n$ coincided with a high $S$. The absolute values of $S$ plotted against $n$ shows the difference in size (diameter) dependence for the PbTe NWs in comparison with the $75$-nm and $217$-nm PbTe NWs reported by Chen et al. [19], which may have result from the increase in carrier concentration $n$ coinciding with the decrease in diameter $d$ in that study.
Figure 3. (a) Temperature dependence of carrier concentration and carrier mobility for the a single-crystal PbTe NWs \((d = 142 \text{ nm})\); (b) Absolute value of the thermoelectric power of various PbTe samples as a function of carrier density; electrons, or holes at room temperature [14]. The solid red stars denote the Pb\(_{1.1}\)Te\(_{0.9}\) samples with 75- and 217-nm diameter wires [19]. The white star with a red outline represents the Pb\(_{1.1}\)Te\(_{0.9}\) sample with a 142 nm diameter.
4. Summary

This study reports the electrical conductivity and thermoelectric power were examined as a function of temperature. The NW exhibited n-type semiconductor behavior, and the thermoelectric power was size-dependent, compared with our previous work [19]. Specifically, the NWs with a shorter diameter yielded greater carrier concentration and lower thermoelectric power.

Acknowledgment

Technical support was provided by the Core Facilities for Nanoscience and Nanotechnology at the Institute of Physics, Academia Sinica in Taiwan.

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