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Thermoelectric Characteristics of A Single-Crystalline Topological Insulator Bi_2Se_3 Nanowire

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Abstract: The discovery of topological insulators (TIs) has motivated detailed studies on their physical properties, especially on their novel surface states via strong spin–orbit interactions. However, surface-state-related thermoelectric properties are rarely reported, likely because of the involvement of their bulk-dominating contribution. In this work, we report thermoelectric studies on a TI bismuth selenide (Bi_2Se_3) nanowire (NW) that exhibit a larger surface/volume ratio. Uniform single-crystalline TI Bi_2Se_3 NWs were successfully synthesized using a stress-induced growth method. To achieve the study of the thermoelectric properties of a nanowire (NW), including electrical conductivity (σ), Seebeck coefficient (S), and thermal conductivity (κ), a special platform for simultaneously performing all measurements on a single wire was designed. The properties of σ, S, and κ of a 200 nm NW that was well precharacterized using transmission electron microscope (TEM) measurements were determined using the four-probe method, the two-probe EMF across ∇T measurement, and the 3ω technique, respectively. The integrated TE properties represented by the figure of merit ZT ($S^2\sigma T/\kappa$) were found to be in good agreement with a theoretical study of Bi_2Se_3 NW.

Keywords: thermoelectric; bismuth selenide; nanowire

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1. Introduction

The study of nanoengineered thermoelectric materials used for converting waste heat into electricity has become a compelling research topic [1–5]. The thermoelectric (TE) generator and the TE sensor are devices that can harvest renewable energy for power generation and thermal sensing, respectively [6–11]. The efficiency of TE materials is determined by the dimensionless figure of merit ZT, which is defined as $S^2\sigma T/(\kappa_e + \kappa_l)$, where S is the TE power or Seebeck coefficient, σ represents the electrical conductivity, κ_e is the electronic thermal conductivity, and κ_l is the lattice thermal conductivity. The quantity $S^2\sigma$ is defined as the power factor (PF). The Weidmann–Franz law restricts the ratio σ/κ in a bulk TE compound. Furthermore, a sharply peaked density of states (DOS) favors a large S, while the density of states in bulk materials is a smoothly variable function. As dimensionality is reduced from three to one, the electronic DOS at the energy-band edges is significantly increased, increasing the TE PF ($S^2\sigma$) and yielding an improved ZT [12,13]. Then, according to Dresselhaus et al., 1D nanowires can boost thermoelectric performance [13,14]. A Bi nanowire would also have a reduced κ due to phonon scattering off the sidewalls, which helps increase ZT, based on a previous study [13,15].

Slack et al. reported that semiconductors exhibiting narrow band gaps and high mobility carriers are optimal TE materials [16]. Bi_2Se_3 is a V–VI topological-insulator material that exhibits a narrow band gap of approximately 0.3 eV and crystallizes in a rhombohedral structure belonging to the tetradymite space group D^5_{3d} (R-3m) [17–19]. This

material demonstrates potential for application in optical recording systems [20], photoelectrochemical devices [21], and TE devices [17,18]. In recent years, bismuth chalcogenides have attracted substantial research interest because of their superior TE properties of high *ZT* at room temperature [22]. Diverse synthesis techniques have been developed to synthesize various nanostructures of Bi_2Se_3, such as microwave heating [23,24], a single-source precursor method [25–27], solvothermal method [28–30], the metal–organic chemical vapor deposition method [31,32], and mechanical exfoliation [33–35], whereas the commonly used synthesis method for producing Bi_2Se_3 bulk single-crystalline material is based on the Bridgman technique [36–41]. However, only a few studies have been reported on growing Bi_2Se_3 NWs and characterizing their TE properties.

2. Materials and Methods

We previously synthesized PbTe NWs from a PbTe thin film (TF) on a SiO_2/Si substrate using a stress-induced method [42,43] based on a mechanism in which mismatched thermal expansion between a substrate and deposited film drove the mass flow along grain boundaries at thermal annealing temperatures. This innovative NW-growth method (which does not involve conventional templates, catalysts, or starting materials) enables us to control growth conditions for growing different diameters, shapes, and aspect ratios of single-crystalline NWs [44,45], thus enabling exploration of any possible novel TE property of Bi_2Se_3 NWs.

The starting Bi_2Se_3 crystalline ingot was synthesized from Bi and Se source materials using the Bridgman method. Bi (99.999%, −200 mesh, Alfa Aesar, Lancashire, UK) and Se (99.999%, −200 mesh, Alfa Aesar, Lancashire, UK) powders were first mixed at a 2:3 ratio and then melted at 800 °C for 4 h in a vacuumed quartz tube at a pressure less than 5×10^{-6} torr. The molten compound was slowly cooled in the furnace to room temperature. Subsequently, a pellet specimen cut from the compound served as the target for pulsed laser deposition (PLD). Single-crystal SiO_2/Si (100) wafers (E-light Tech. Inc. Taipei, Taiwan; SiO_2 thickness = 1μm; diameter = 100 ± 0.5 mm) with double-side polishing were cut into 1.5 × 1.5 cm^2 squares for substrates. All substrates were cleaned using acetone, isopropyl alcohol, and deionized water in an ultrasonic bath for 10 min before being dried with an N_2 stream. The Bi_2Se_3 films were fabricated using an ArF excimer laser (Lambda Physik LPXPro 210, Santa Clara, California, USA) and deposited onto substrates in a vacuum system with a base pressure of 5.0×10^{-7} torr. The Bi_2Se_3 TFs were grown at a deposition rate of 0.3 Å/s, and 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 film thickness was 30 nm. The films were sealed in a vacuumed quartz tube at less than 5×10^{-6} torr for annealing at 450 °C for 5 d, followed by cooling the furnace to room temperature. During the annealing process, Bi_2Se_3 NWs grew from the film via the different thermal expansion coefficients of the Bi_2Se_3 film (19×10^{-6}/°C) [46] and the SiO_2/Si substrate (0.5×10^{-6}/°C)/(2.4×10^{-6}/°C) [42–45].

3. Results and Discussion

3.1. Characterization of Materials

Field emission scanning electron microscopy (Hitachi Co., S-4800, Tokyo, Japan) images of the Bi_2Se_3 NWs (Figure 1a) showed that the NWs exhibited diameters ranging from 50 to 500 nm and lengths up to 100 μm. Straight and uniform Bi_2Se_3 NWs of high aspect ratio grew on the substrate after annealing. A tungsten needle (*d* = 100 nm) and a binocular optical microscope were used to extract a single-crystal NW from the Bi_2Se_3 film; the NW was then suspended on a Si_3N_4 microchip by using electrodes (Figure 1b) and employed in structural analyses and thermoelectricity measurements. A transmission electron microscope (TEM; JEOL JEM-2100 at 200 kV, Tokyo, Japan) was used to examine the crystalline structure of the Bi_2Se_3 NW (Figure 1c,d).

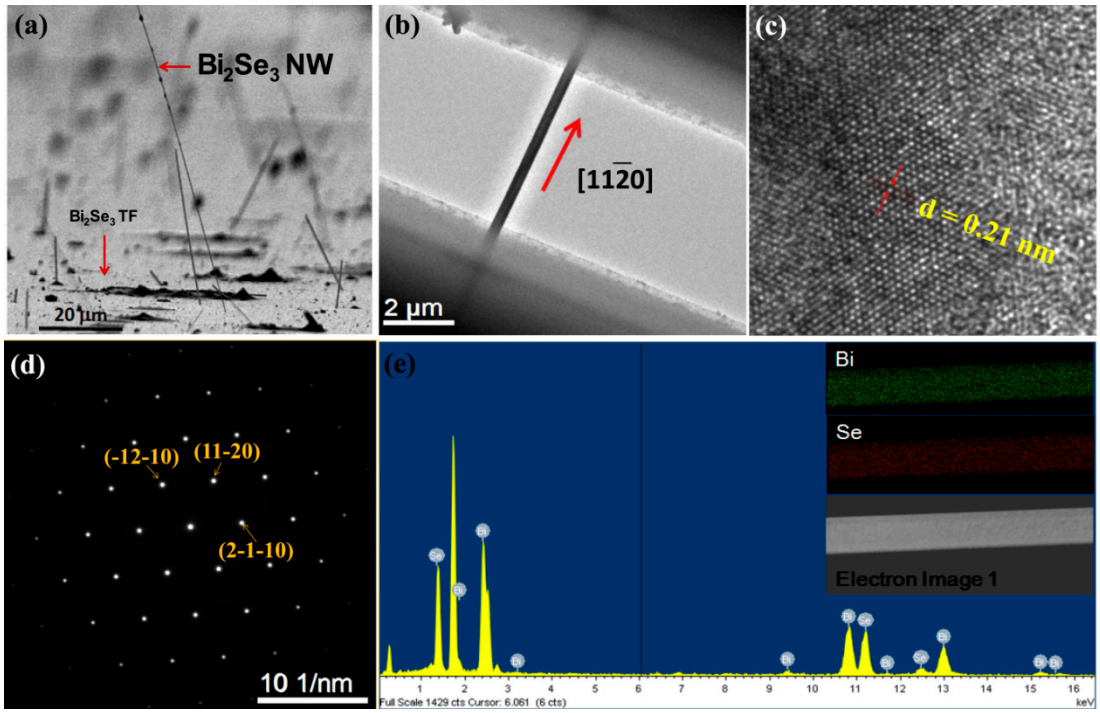

Figure 1. (**a**) SEM image (top view) indicating that all Bi_2Se_3 NWs grew several micrometers in length from the surface of the Bi_2Se_3 TF; (**b**) TEM images of a single-crystal Bi_2Se_3 NW suspended on a Si_3N_4 microchip following electrode formation by using a FIB that served as the TEM holder; (**c**) HR-TEM image of the NW shown in (**b**), where the distance between crystal faces is 0.21 nm; (**d**) the SAED pattern (at the [0001] zone axis), confirming that the single-crystalline NWs grew in the [11–20] direction; and (**e**) EDS spectrum of a Bi_2Se_3 NW (the inset shows the EDS mapping image of a NW).

The electrical resistivity ρ and Seebeck coefficient S of the Bi_2Se_3 bulk were measured simultaneously using commercial equipment (ZEM-3, ULVAC-RIKO, Chigasaki, Kanagawa, Japan) in a He atmosphere from 300 to 540 K. The thermal conductivity κ of the Bi_2Se_3 bulk was calculated using the equation $\kappa = D.C_p.d$, where D is the thermal diffusivity, C_p is the specific heat, and d is the density of the sample. The thermal diffusivity D was examined via a laser-flash apparatus (NETZSCH, LFA 457, Selb, Germany), and the density d was obtained using the Archimedes method (presented in Figure S1, electronic supporting information (ESI)). The Seebeck coefficient S and the electrical resistivity ρ of an NW were measured using a conventional steady-state method in an Oxford cryostat. The NW thermal conductivity was measured using the 3ω method.

The TEM image (TEM; JEOL JEM-2100 at 200 kV, Tokyo, Japan) in Figure 1c reveals that the ordered hexagonal structure exhibiting lattice fringes of 0.21 nm gaps between the [11–20] planes were consistent with those of other lattice spacing measurements of Bi_2Se_3 NWs [47]. A corresponding selected area electron diffraction (SAED) pattern (Figure 1d) reveals that the Bi_2Se_3 NWs were high-quality single crystals that exhibited growth along the [11–20] direction. The chemical composition of the Bi_2Se_3 NW was examined using energy dispersive X-ray spectroscopy (EDS, JEOL, Tokyo, Japan); the EDS mapping shown in the inset of Figure 1e indicates the uniform spatial distribution of Bi and Se elements throughout the NW.

Figure 2 shows a SEM image of a Bi_2Se_3 NW (d = 200 nm) suspended on a Si_3N_4 microchip between 10 nm Ni/50 nm Au electrodes and a Pt/C electrical contact deposited by a focus ion beam (FIB). The sample used in this study showed nearly an ohmic contact. Subsequently, the microchip was used to determine the values of electrical resistivity ρ and S via four-point measurements.

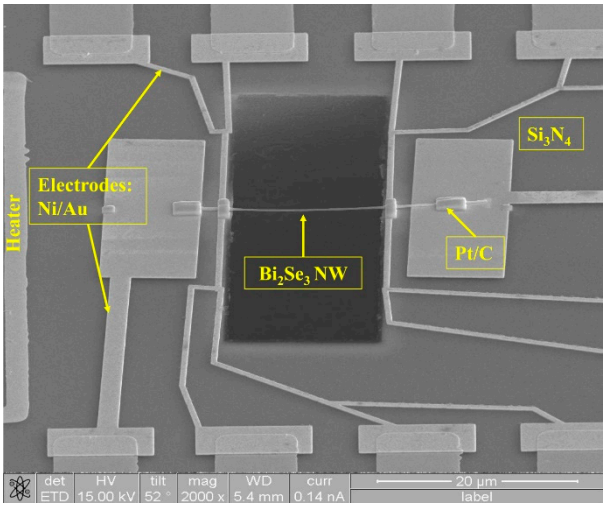

Figure 2. The SEM image of a single-crystal Bi_2Se_3 NW (diameter = 200 nm) placed on a Si_3N_4 microchip following electrode formation by using a FIB.

3.2. Characterization of Thermoelectric Properties

Figure 3a shows the temperature dependence of the electrical resistance at 290–320 K for a 200 nm Bi_2Se_3 NW that exhibited weak metallic conductivities. The σ of the NW at near room temperature was 1.50767×10^5 S m^{-1} (Figure 3b), which was approximately 55% lower than that of the Bi_2Se_3 bulk single-crystal (2.7550×10^5 S m^{-1}) [41] (Table 1). Furthermore, the surface scattering of charge carriers typically yields a reduced σ value [48]. However, the σ values of the Bi_2Se_3 NW at room temperature was higher than those reported in previous studies on the Bi_2Se_3 bulk [23–26,28,29,32], and even higher than that of the Bi_2Se_3 single-crystal made by Hor et al. [39], probably the result of the increased contribution of conduction surfaces up to 73% of the total electrical conduction upon decreasing the NW dimension via the high surface-to-volume ratio s/v ~ 2 nm^{-1} of the nanowires. A previous report [19] of electrical transport experiments on Bi_2Te_3 and Bi_2Se_2Te nanowires in the range of 200–300 nm in diameter revealed that the two-dimensional TI surface channels contribute up to 30–70% of the total electrical conduction at surface-to-volume ratios of s/v = $2-5 \times 10^{-2}$ nm^{-1}.

The *S* values with the negative sign obtained for the Bi_2Se_3 NW (Figure 3c) show that the Bi_2Se_3 NW is an n-type semiconductor, because electrons have much higher mobility than holes and dominate the transport [49,50]. This is reasonable because undoped Bi_2Se_3 is strongly n-type [51]. Furthermore, the room temperature *S* values for the *n*-type Bi_2Se_3 NW was -51 µVK^{-1} for the 200 nm NW, the value was comparable to those typically reported by Greenaway and Harbeke for this material (i.e., in the -55 to -73 µVK^{-1} range) [52], indicating that the Fermi level lay well inside the conduction band. The magnitude of the *S* smoothly increased as the temperature increased. This behavior was consistent with that expected of a metallically doped material. The magnitude of *S* for the NW tends to be zero when the temperature is decreased because *S* represents the entropy per electric charge and must decrease to zero at 0 K [15]. Figure 3d indicates the temperature dependence of the *PF* of Bi_2Se_3 NW, indicating that the *PF* increased as temperature increased; this can be attributed to the increase in the *S* with the temperature of the Bi_2Se_3 NW. The *PF* value of the 200 nm Bi_2Se_3 NW at room temperature was 39.32×10^{-5} Wm^{-1}K^{-2}, which was higher than the *PF* of the Bi_2Se_3 bulk nanostructures [21–24,26,27,31]. The enhanced *PF* value is likely a result of enhanced electronic transport of the NW.

For semiclassical transport (metals or degenerate semiconductors) the carrier-density dependence of the thermopower is described by the Mott relation [53–55]:

$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m^* \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \quad (1)$$

where k_B is Boltzmann's constant, q is the electron charge, h is Planck's constant, T is the measurement temperature, m^* is the effective mass of the carrier (m^* = 0.14 m_o in Bi_2Se_3) [56] and m_o is the electron mass. This formula is valid for assessing metals or degenerate semiconductors that exhibit an n value in the range of 10^{18} to 10^{20} cm^{-3} [57,58]. The value of n is in the range of 1.26–1.35 × 10^{19} cm^{-3} at 290–320 K for the 200 nm NW (Figure 4), indicating that the NW is a degenerate semiconductor. This value is close to that calculated by Boechko et al. for n-type single crystals of a Bi_2Se_3 single crystal (1–4 × 10^{19} cm^{-3}) [59]. The value of n increased as the temperature increased, indicating the intrinsic condition [60], with the number of thermally generated carriers exceeding the number of donor carriers. The intrinsic carrier concentration in a material n_i is generally much smaller than the dopant carrier concentration at room temperature, but n_i (=$n \cdot p$) has a very strong temperature dependence:

$$n_i \propto T^{1.5} e^{-\frac{E_{g0}}{2kT}} \quad (2)$$

where E_{g0} is the energy band gap at T = 0 K [60].

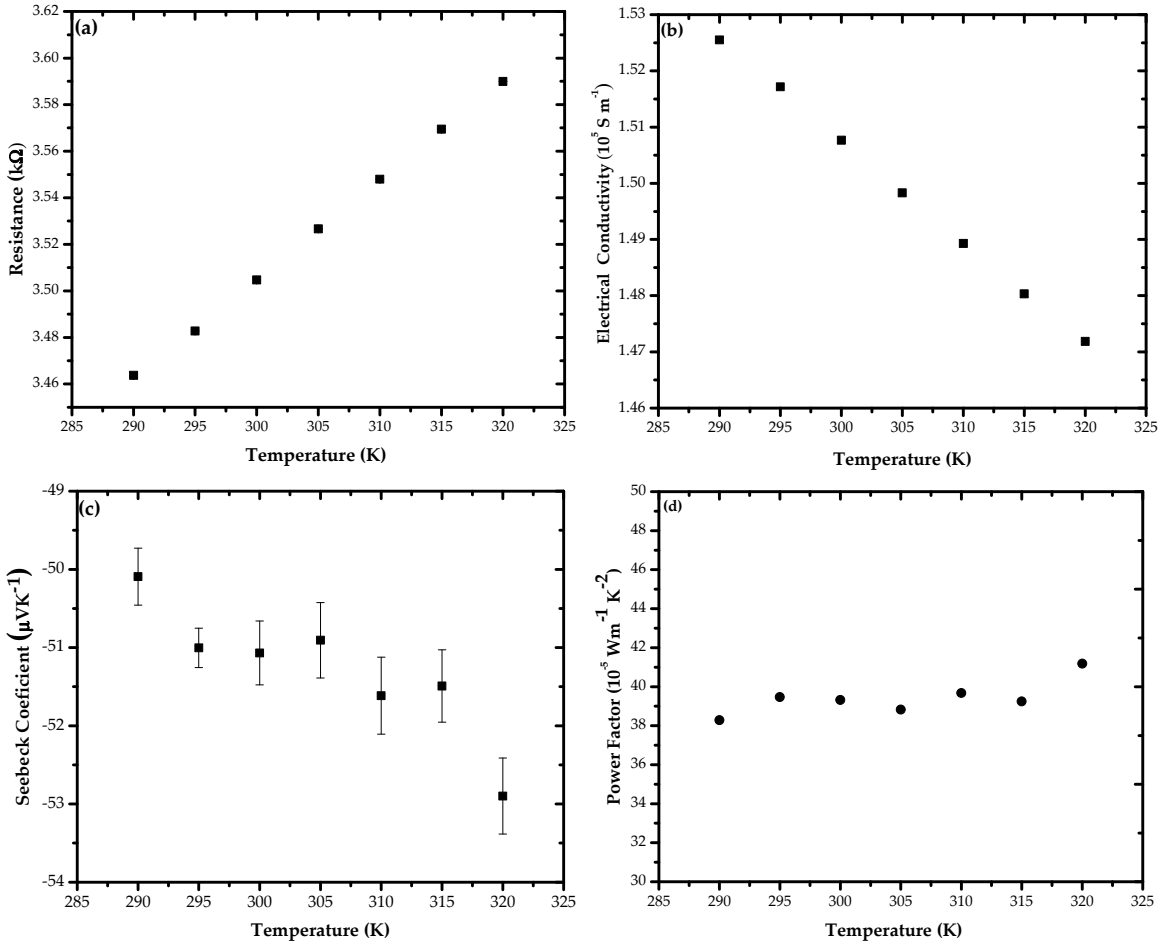

Figure 3. Temperature dependence regarding the (**a**) electrical resistance, (**b**) electrical conductivity, (**c**) TE power (S) and (**d**) power factor of the single-crystal Bi_2S_3 NW.

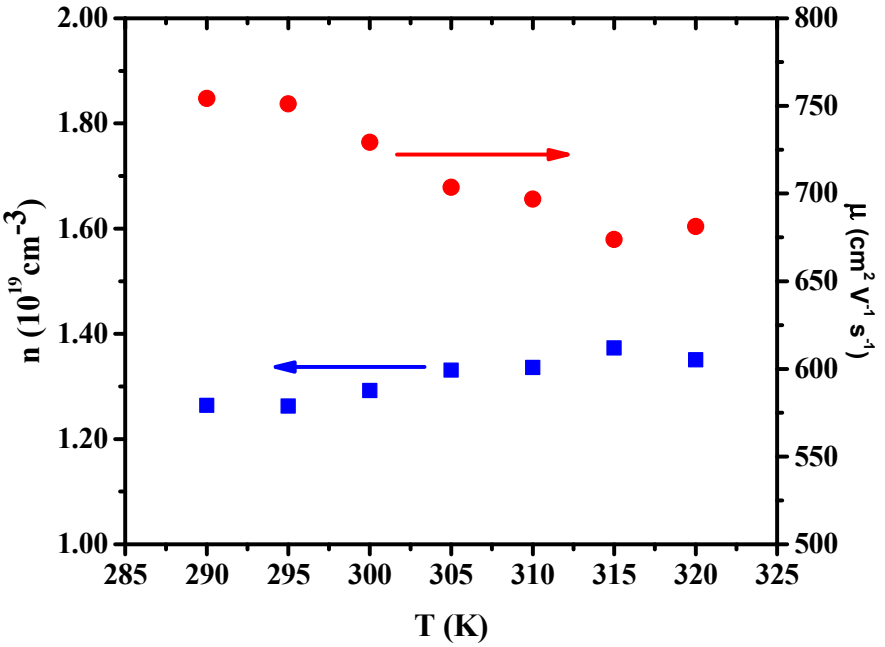

Figure 4. Temperature dependence of carrier concentration and carrier mobility for Bi_2Se_3 NW.

Figure 4 also depicts the calculated T dependences of carrier mobility μ for the Bi_2Se_3 NW. The μ value is obtained using the following equation:

$$\mu = \frac{1}{\rho n q} = \frac{\sigma}{nq} \tag{3}$$

Our calculated values of μ at 290–320 K were 754–681 cm^2 V^{-1} s^{-1} for the 200 nm NW; these values were much smaller than those of the Bi_2Se_3 bulk (approximately 920–1060 cm^2 V^{-1} s^{-1}) [41], but higher than those reported by Le et al. [60] for Bi_2Se_3 TFs (7.2 ± 0.2 to 98.4 ± 0.5 cm^2 V^{-1} s^{-1}). The μ values decreased as temperature increased because of the phonon concentration increase that caused increased scattering. Thus, lattice scattering reduced the carrier mobility at higher temperature. The mobility of a semiconductor depends on the impurity concentrations (including donor and acceptor concentrations), defect concentration, temperature, and electron and hole concentrations.

The primary factor involved in determining μ in the semiconductor is the scattering mechanism through the relation $\mu_j \propto T^{\alpha}$ [61]. Conduction carriers are scattered by acoustic phonons μ_l when $\alpha = -\frac{3}{2}$, whereas they are scattered by ionized impurities μ_i when $\alpha = \frac{3}{2}$. The μ values of the 200 nm Bi_2Se_3 NW continually decreased as the T increased, indicating that phonon scattering was dominant throughout the whole temperature range.

The thermal conductivity of Bi_2Se_3 NW was measured by the self-heating 3ω method in the temperature range of 290–320 K. The 3ω signal can be expressed as [62,63]:

$$V_{3\omega} = \frac{4I_0^3 LRR'}{\pi^4 \kappa S \sqrt{1 + (2\omega\gamma)^2}} \tag{4}$$

where I and ω are the amplitude and frequency of the alternating current applied on the nanowire, respectively; R and R' are the resistance and derivative of resistance at the corresponding temperature, respectively; κ is the thermal conductivity; S is the NW cross-section area; and γ is the characteristic thermal time constant. Figure 5a shows the current dependence of $V_{3\omega}$ at 300 K, demonstrating an I_0 dependence in an intermediate current range; one can see that $V_{3\omega}(I_0)$ followed the ${I_0}^3$ dependence well, in agreement with Equation (4). Figure 5b,c show the frequency dependencies of the amplitude and the

phase angle of $V_{3\omega}$ at 300 K, respectively, compared with the predicted functional forms (the solid lines). The fitting parameters for Figure 5a,b are shown in Tables S1 and S2, respectively.

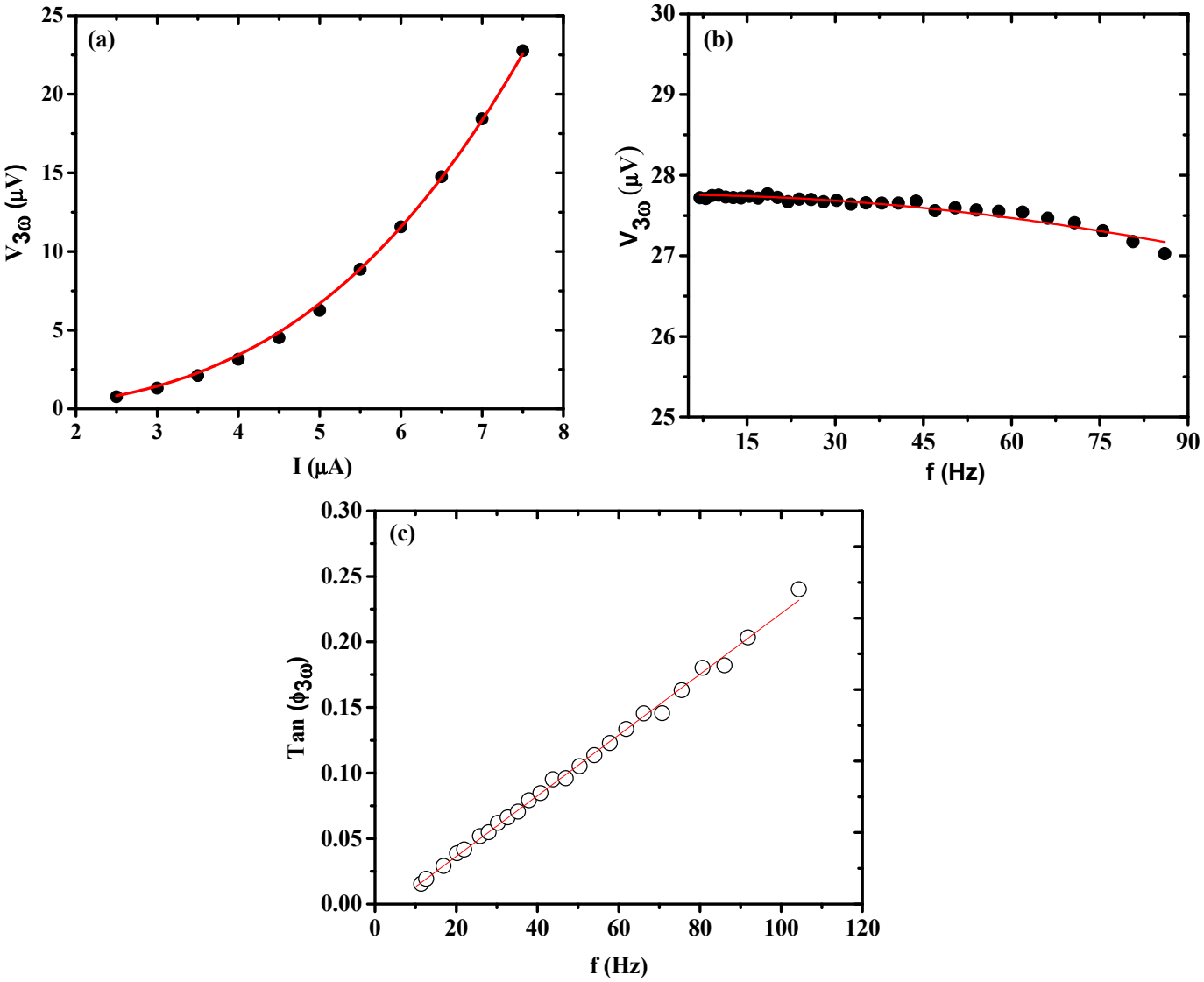

Figure 5. (**a**) The third harmonic voltage signal V3ω as function of the extraction current amplitude I_o. The solid line shows the cubic relationship of V3ω and I_o. (**b**) Frequency dependence of V3ω. The solid line is the predicted relation $V3\omega \propto 1/\sqrt{1+(2\omega\gamma)^2}$. (**c**) The frequency dependence of the phase angle of V3ω at 300 K of Bi_2Se_3 NW; d = 200 nm.

By fitting the data in Figure 5a to equation $V_{3\omega} = \frac{4I_0^3 LRR'}{\pi^4 \kappa S}$ ($\omega\gamma \rightarrow 0$), we obtained the thermal conductivity κ, and the thermal time constant γ was ~2 ms at 300 K, comparable to a simple theoretical calculation of κ based on the Callaway model for nanostructured Bi_2Se_3 made by Li et al. [64,65]. It is known that phonon-boundary scattering can suppress the thermal conductivity in nanowires [66,67]. However, the data on a Bi_2Se_3 NW with d = 200 nm from the experimental κ values (κ = 2.02 to 2.09 W m^{-1} K^{-1} at 290–320 K) as plotted in Figure 6a are in reasonable agreement with the Callaway model between the κ values of 300 nm (κ > 2 W m^{-1} K^{-1}) and 100 nm (κ < 2 W m^{-1} K^{-1}) [64]. The measured thermal conductivity, given by the κ value (κ is measured perpendicular to c plane) at T = 300 K of the NW (2.05 W m^{-1} K^{-1}) was ~33% lower than those for Bi_2Se_3 bulk single-crystal (2.96 W m^{-1} K^{-1} or 3.1 W m^{-1} K^{-1} in Table 1) [39,41].

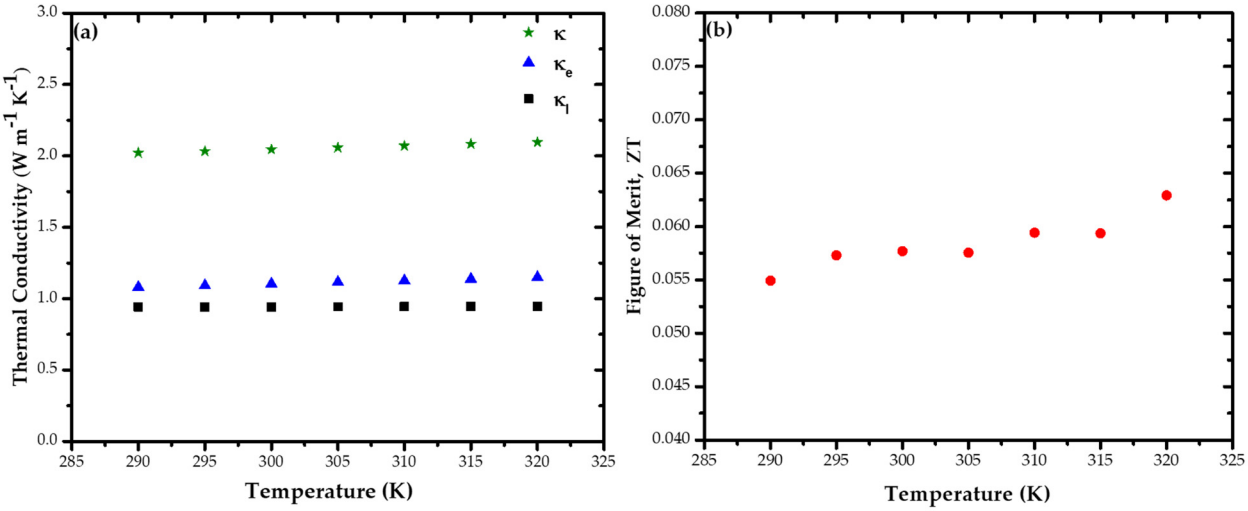

Figure 6. (**a**) Thermal conductivity κ, and (**b**) figure of merit *ZT* values of Bi_2Se_3 NW in the temperature range of 290 K to 320 K.

Table 1. The transport properties of Bi_2Se_3 nanowire and bulk at room temperature.

Sample *	S [μV K^{-1}]	Σ [S m^{-1}]	PF [10^{-5} W m^{-1}K^{-2}]	κ W m^{-1}K^{-1}	ZT	Ref.
Bi_2Se_3	−53	38678	10.70	0.78	0.04	[26]
Bi_2Se_3	−115	212	2.80	0.75	0.01	[28]
$Bi_2Se_{2.83}$	−60	25000	9	0.55	0.05	[29]
Bi_2Se_3 Nanowire SC (φ = 200 nm)	−51	150767	39.32	2.05	0.06	Our Work
Bi_2Se_3 Bulk SC	−62.10	259998	100	1.55	0.19	Our Work
Bi_2Se_3 Bulk SC	−190	47619	172	2.96	0.17	[39]
Bi_2Se_3 Bulk SC	−59	275500	95.90	3.1	0.09	[41]

* SC = single-crystalline.

The electronic thermal conductivity κ_e values of the Bi_2Se_3 NWs here were calculated according to the Wiedemann–Franz law:

$$\kappa_e = L\sigma T \quad (5)$$

where *L* is the Lorenz number (2.44×10^{-8} W Ω K^{-2}). When subtracting the κ_e values from the measured thermal conductivity, one obtains the phonon (or lattice) part of the thermal conductivity as $\kappa_l = \kappa\text{-}\kappa_e$. The temperature-dependent data for κ_l thus obtained are shown in Figure 6a. The obtained for κ_l and κ_e at 300 K for NWs were 29% and 37% lower than that of the Bi_2Se_3 bulk single-crystal (κ_l = 1.33 W m^{-1} K^{-1} and κ_e = 1.77 W m^{-1} K^{-1}) [41]. The thermal conductivity was dominated by the electronic contribution in the 290–320 K range, although Birkholz and Rosi both reported a value for κ_l of Bi_2Se_3 bulk of between 2.0 and 2.4 W m^{-1} K^{-1} [51]. It was shown that the large surface-to-volume ratio s/v of nanowires could enhance phonon surface scattering and decrease κ_l.

Additionally, for this nanowire, *ZT* calculated from the obtained *S*, σ, and κ was approximately 0.06 at 300 K (Figure 6b). However, the *ZT* values of this nanowire were still higher than those of Bi_2Se_3 bulk used to construct nanostructures at 290–320 K, as reported previously [26,28,29]. Table 1 shows a summary of the transport properties of single-crystalline Bi_2Se_3 NW, compared with those reported Bi_2Se_3 bulk at room temperature. Our *S*, σ, and κ results of Bi_2Se_3 NW *d* = 200 nm were in reasonable agreement with a theoretical study [19]. This agreement indicates the high-quality crystallinity of the Bi_2Se_3 NWs grown by the stress-induced method.

4. Conclusions

The stress-induced method was applied to grow single-crystalline Bi_2Se_3 nanowires (NWs) from a Bi_2Se_3 TF on a SiO_2/Si substrate, offering an alternative technique for Bi_2Se_3 NWs synthesis without a catalyst. This technique had not been previously applied to

Bi_2Se_3 alloys. In this work, at room temperature, the Bi_2Se_3 nanowire (NW) (d = 200 nm) exhibited a *PF* of approximately 39.32 × 10^{-5} $Wm^{-1}K^{-2}$, which was higher than that reported for Bi_2Se_3 bulk nanostructures; this discrepancy was mainly attributed to the electron-transport contribution of this NW. The measured thermal conductivity κ value of a NW was 2.05 W m^{-1} K^{-1}, which was 31−34% lower than those for a Bi_2Se_3 bulk single crystal [39,41] because of the electron-scattering contribution. The figure of merit *ZT* value of Bi_2Se_3 NW rose up to approximately 0.06 at room temperature, in agreement with a theoretical study of the thermoelectric properties on a topological insulator of Bi_2Se_3 NWs [19]. Our results indicated that NWs grown using the stress-induced method yield high-quality single crystals.

Supplementary Materials: The following are available online at https://www.mdpi.com/2079-4991/11/3/819/s1, Figure S1: (a) Image of Bi_2Se_3 single-crystalline grown by the Bridgman method. (b) The measured thermoelectric properties were −62.10 μ VK^{-1}, 259998 S m^{-1}, 1.55 W m^{-1} K^{-1}, and 0.19 for the Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ) and figure of merit *ZT*, respectively, at room temperature, as shown in Table 1, Table S1: The fitting parameters of the third harmonic voltage signal V3ω as function of the extraction current amplitude Io for Figure 5a, Table S2: The fitting parameters of frequency dependence of V3ω for Figure 5b.

Author Contributions: Conceptualization, D. and Y.-Y.C.; methodology, D., P.-C.W. and P.-C.L.; software, D. and P.-C.L.; validation, D. and Y.-Y.C.; formal analysis, D., P.-C.L. and Y.-Y.C.; investigation, D., P.-C.L. and Y.-Y.C.; resources, D., P.-C.W. and P.-C.L.; data curation, D., P.-C.L. and Y.-Y.C.; writing—original draft preparation, D.; writing—review and editing, D., P.-C.L. and Y.-Y.C.; visualization, D.; project administration, P.-C.L. and Y.-Y.C.; supervision, Y.-Y.C.; funding acquisition, D. and Y.-Y.C., All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflict of interest.

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