Article

Optical and Thermoelectric Properties of Surface-Oxidation Sensitive Layered Zirconium Dichalcogenides ZrS$_{2-x}$Se$_x$ (x = 0, 1, 2) Crystals Grown by Chemical Vapor Transport

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Abstract: In this work, structure, optical, and thermoelectric properties of layered ZrS$_{2-x}$Se$_x$ single crystals with selenium composition of x = 0, 1, and 2 were examined. Single crystals of zirconium dichalcogenides layer compounds were grown by chemical vapor transport method using I$_2$ as the transport agent. X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM) results indicated that ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) were crystalized in hexagonal CdI$_2$ structure with one-layer trigonal (1T) stacking type. X-ray photoelectron and energy dispersive X-ray measurements revealed oxidation sensitive behavior of the chalcogenides series. Transmittance and optical absorption showed an indirect optical gap of about 1.78 eV, 1.32 eV, and 1.12 eV for the ZrS$_{2-x}$Se$_x$ with x = 0, 1, and 2, respectively. From the result of thermoelectric experiment, ZrSe$_2$ owns the highest figure-of-merit (ZT) of ~0.085 among the surface-oxidized ZrS$_{2-x}$Se$_x$ series layer crystals at 300 K. The ZT values of the ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series also reveal increase with the increase of Se content owing to the increase of carrier concentration and mobility in the highly Se-incorporated zirconium dichalcogenides with surface states.

Keywords: 2D semiconductor; surface state; thermoelectric material; optical property

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) as MX$_2$ (M = Mo, W, Re and X = S, Se) [1–5] and III-VI layer compounds as NX (N = Ga, In and X = S, Se) [6–8] have recently received considerable attentions on their excellent optical and electrical properties available for application in electronics and optoelectronics devices [9] because their specific characteristics of flexible, large-area, and ultra-thin, etc. These materials have a proper band gap of 1~2.5 eV (in near infrared to visible region) [10,11] that suitable for solar-energy applications. Among them, III-VI GaSe and GaS series showed feasibility for making visible light emitting devices owing to their widened and adjustable band gaps [10,11]. On the other hand, ZrX$_2$ (X = S, Se) are the group IVB TMDC materials that crystallized in one-layer trigonal (1T) structure of CdI$_2$ type [12]. These materials also have band gaps ranging from 1.1 to 2 eV [13,14]. The compounds usually possess high conductivity and contains defects and surface states in its layer structure. The proper band-gap value and higher conductivity may also render ZrX$_2$ suitable for electronic and thermoelectric device applications [15–17]. Despite their TMDC counterparts of MoS$_2$ series undergoing an indirect-to-direct band gap transition in the monolayer form [18], the ZrX$_2$ series TMDCs may remain in indirect band gap in all thicknesses [19]. The electronic band gaps and optical properties of the layered ZrX$_2$ (X = S, Se) series compounds are rarely studied up to date.
In earlier research, the first principle thermoelectric properties of zirconium dichalcogenides was reported by a number of authors [20,21]; nevertheless, experimental works on thermoelectric properties of ZrX₂ (X = S, Se) have rarely been reported. Some of the 1D nanowire and nanoscale thermoelectric materials have been claimed to have improved thermo-electronic transport property [22,23]; however, to date, experimental thermoelectric measurements on the Zr-based ZrSₓ, ZrSe, and ZrSe₂ layered TMDCs are seldom found in the literature, in spite of some thermoelectric materials [24–27] having been reported for power-generation applications. In this paper, the optical and thermoelectric properties of ZrS₂₋ₓSeₓ (x = 0, 1, and 2) were characterized using temperature-dependent transmittance, Raman, and thermoelectric measurements from low to room temperature. Transmittance and optical absorption revealed indirect allowed transition of all series ZrS₂₋ₓSeₓ (x = 0, 1, and 2) layered crystals. Raman measurement of ZrS₂₋ₓSeₓ (x = 0, 1, and 2) also sustains that the whole series 2D materials are crystallized in the 1T phase similar to the result of X-ray diffraction (XRD). The Raman mode of A₁₆ is the prominent peak in the layer plane. Because of surface oxidation, the ZrS₂₋ₓSeₓ (x = 0, 1, and 2) series chalcogenides reveal lower resistivity. From thermoelectric measurement, the ZT value increases with the Se content is increased in the ZrSe₂₋ₓSeₓ (x = 0, 1, and 2) series at room temperature.

2. Materials and Methods

High quality ZrS₂₋ₓSeₓ (x = 0, 1, and 2) bulk crystals were grown by chemical vapor transport (CVT) method using iodine (I₂) as the transport agent [28]. Prior to the growth, synthesis of the starting material powders of ZrS₂₋ₓSeₓ (x = 0, 1, and 2) with stoichiometry were needed. For crystal growth, the starting material powder together with proper amount of transport agent (10 mg/cm³) were cooled with liquid nitrogen, and then sealed in a vacuum of ~10⁻⁶ Torr inside a quartz ampoule. The growth temperature was set as 900 °C → 850 °C with a gradient of 2.5 °C/cm. The growth time kept 280 h for growing single crystals. After the growth the crystal series essentially exhibited silver-black and shiny color on their fresh surface. When they are oxidized in ambient (about 8 days in air) ZrS₂ becomes silver-yellow color, ZrSSe becomes silver orange, and ZrSe₂ becomes silver red. The color change is maybe caused by free of chalcogen (S, Se) and which substitution by oxygen in the zirconium compounds. The crystal images are shown in Figure S1 in supporting information (SI) for contrast. With weakened van der Waals bonding between the layers, thin ZrX₂ nanosheets can be mechanically exfoliated and transferred onto a SiO₂/Si substrate (8 × 8 × 0.3 mm³) using Scotch tape for performing micro-Raman experiment. To avoid surface oxidation in air, the as-grown ZrX₂ series crystals and exfoliated nanosheets (on SiO₂/Si) were stored in an evacuated chamber before measurements. Prior to each of the experiments, the as-grown crystals can be exfoliated again to obtain fresh surface.

For X-ray diffraction (XRD) measurements, several small crystals from each composition of the ZrX₂ series were finely ground and the X-ray powder patterns were taken and recorded by means of a slow moving radiation detector. The copper Kα radiation (1.542 Å) was employed in the X-ray diffraction measurements, and a silicon standard was used for experimental calibration. The micro-Raman measurements of the ZrS₂, ZrSe, and ZrSe₂ nanosheets were carried out in a RAMaker microscope spectrometer (ProTrustTech, Tainan, Taiwan) with a 532-nm solid state diode-pumped laser as the excitation source. An Olympus objective lens (50× or 100× with long working distance) acted as the interconnection-coupled medium between the nanosheet sample, incident and reflected lights, and a charge-coupled-device (CCD) spectrometer equipped with one 1200 grooves/mm grating. The power of the 532-nm laser was controlled at 8 mW and the spot size was ~0.8 μm. A Janis liquid helium open-circled cryostat equipped (Janis Co., Woburn, MA, USA) with Lakeshore 335 digital thermometer controller facilitated low-temperature and temperature-dependent measurements.

For transmission measurement of the thin ZrX₂ (X = S, Se) samples, a 150 W tungsten halogen lamp was utilized for the white light source. The white light was dispersed by a Photonics International (PTI) monochromator (Photonics International, MA, USA) equipped one 600 grooves/mm grating for providing monochromatic light. The incident light was chopped at 200 Hz, and phase-locked detection.
by using a lock-in amplifier was employed. The transmission light from the layer sample was detected by a Si detector (E > 1.1 eV) or an InGaAs detector (E = 0.7 to 1.7 eV) in different wavelength range.

For thermoelectric measurement, a stainless-steel plate of 4 \times 2 \times 0.01 \text{ cm}^3 covered with thin insulating tape on its top surface acted as the sample holder. The insulating tape should have much lower thermal conductivity than the measured sample, to avoid any parasitic heat loss to the substrate. Gold evaporated film on the insulating tape acted as the heater (R \sim 9 \text{ \Omega}) for the layered samples. The layered zirconium dichalcogenide crystals were prepared in rectangle shape of bar-type four-point measurement configuration (size \sim 0.45 \times 0.12 \times 0.01 \text{ cm}^3) that available for both resistivity and thermoelectric measurements. For thermoelectric measurement, one end of the bar-shape ZrX₂ sample was closely attached on the Au-film heater, and a current of \sim 0.4 \text{ A} was sent. When the sample temperature is balanced (after seconds), the voltage difference (\Delta V) and temperature difference (\Delta T) are simultaneously measured from the two central probes of the bar-shape ZrX₂ sample for the estimation of Seebeck coefficient and thermal conductivity. A pair of E-type thermocouples was used for sensing the temperature difference between the two central probes in the thermoelectric-measured sample. The temperature-dependent thermoelectric measurement was done from 20 to 300 K.

3. Results and Discussion

3.1. Structure and Composition Analysis of ZrSₓ₋ₓSeₓ (x = 0, 1, and 2) Crystals

Figure 1a shows high-resolution-transmission-electron-microscope (HRTEM) images of ZrSₓ₋ₓSeₓ (x = 0, 1, and 2) series crystals. The obvious dotted pattern in selected-area-electron-diffraction (SAED) pictures that proves all the crystals are high-quality single crystals. From the HRTEM and SAED results, the lattice constant \(a\) can be determined to be 3.651 Å for ZrS₂, 3.687 Å for ZrSSe, and 3.769 Å for ZrSe₂, respectively. Essentially, the lattice constant \(a\) will be expanded when more Se atoms are incorporated into the ZrSₓ₋ₓSeₓ (x = 0, 1, and 2) series crystals. This result is well-matched with those obtained and calculated from XRD measurement (see Table S1). The XRD results shown in Figure 1b also indicate that ZrSSe series crystals are mainly crystallized in the 1T-CdI₂ layer structure with verification of the preferred \(c\) plane peak indexed as (001) \[29\]. The lattice constant \(c\) measured from XRD can be determined to be 5.818 Å for ZrS₂, 5.980 Å for ZrSSe, and 6.101 Å for ZrSe₂, respectively. For the lattice constant of \(a\) axis, the peak indices of (101), (102), (110), (103), (201), (202), and (113) planes also show gradually increase with the selenium content is increased in the XRD pattern in Figure 1b. This result reveals lattice dilation of \(a\) axis in the ZrSₓ₋ₓSeₓ lattice from \(x = 0\) to \(x = 1\). The monolayer of 1T-ZrX₂ consists of six hexagonal chalcogen atoms that octahedrally coordinated with one center metal atom \[30\]. The obtained lattice constants of ZrSₓ₋ₓSeₓ (x = 0, 1, and 2) reveal that the lattice constant \(a\) possesses the similar trend as that of \(c\), in which the values are simultaneously increased with the Se content is increased as displayed in Figure 1c. For ZrX₂, the metal atoms are located in the centre sheet and which is sandwiched by two chalcogen layers to form X-M-X monolayer with strong covalent bond within the layer plane, and adjacent layers are connected by weak van der Waals force as displayed in Figure 1d \[19,31\]. All the structural analysis of HRTEM and XRD in Figure 1 confirmed that the ZrSₓ₋ₓSeₓ (x = 0, 1, and 2) series crystals are crystallized in the 1T layered structure.
the layer sample was detected by a Si detector (E > 1.1 eV) or an InGaAs detector (E = 0.7 to 1.7 eV) in different wavelength range. For thermoelectric measurement, a stainless-steel plate of 4×2×0.01 cm−3 covered with thin insulating tape on its top surface acted as the sample holder. The insulating tape should have much lower thermal conductivity than the measured sample, to avoid any parasitic heat loss to the substrate. Gold evaporated film on the insulating tape acted as the heater (R ~ 9Ω) for the layered samples. The layered zirconium dichalcogenide crystals were prepared in rectangle shape of bar-type four-point measurement configuration (size ~0.45×0.12×0.01 cm3) that available for both resistivity and thermoelectric measurements. For thermoelectric measurement, one end of the bar-shape ZrX2 sample was closely attached on the Au-film heater, and a current of ~0.4 A was sent. When the sample temperature is balanced (after seconds), the voltage difference (ΔV) and temperature difference (ΔT) are simultaneously measured from the two central probes of the bar-shape ZrX2 sample for the estimation of Seebeck coefficient and thermal conductivity. A pair of E-type thermocouples was used for sensing the temperature difference between the two central probes in the thermoelectric-measured sample. The temperature-dependent thermoelectric measurement was done from 20 to 300 K.

Figure 1. (a) High-resolution transmission electron microscope (HRTEM) results, selected-area-electron-diffraction (SAED), and FFT images of ZrS2, ZrSSe, and ZrSe2. (b) XRD pattern of ZrS2−xSex (x = 0, 1, and 2). (c) Selenium doping effect on the variation of lattice constants a and c. (d) Atomic arrangements of layered ZrX2 (X = S, Se) observed from top view and side view.

Energy dispersive X-ray (EDX) spectroscopy is carried out to estimate stoichiometric content of ZrS2−xSex (x = 0, 1, and 2) series (Figure S2). The x value of chalcogen composition is lower than that of nominal composition due to the surface oxidation under ambient air condition after eight days. The ZrSe2 demonstrate color change due to the surface oxidation as evident in Figure S1b,c from black shiny (fresh surface) to pink red and white color (oxidize surface). It is noticed that even with fresh surface, the ZrX2 samples in Figure S2 still revealed chalcogen deficiency, the zirconium dangling bonds can easily oxidize with oxygen in the layer compounds. Thus, the surface states and defects, like S/Se vacancies or Zr interstitials, still exist in the ZrS2−xSex to affect electrical conduction and carrier transport properties. These layered semiconductors will become degenerate and high carrier concentration, and we will evaluate the materials by temperature-dependent resistivity later.

3.2. Raman Spectroscopy

For micro-Raman measurement, the bulk ZrS2−xSex (x = 0, 1, and 2) samples are exfoliated into thin layers (t < 40 nm, measured by atomic force microscopy) on a commercialized SiO2/Si substrate (thickness: SiO2~200 nm and Si~300 µm). The ZrX2 thin layers were characterized from 4 to 300 K. Figure 2a shows the Raman spectra of multilayer ZrS2−xSex (x = 0, 1, and 2) at room temperature.
and the low temperature Raman spectra at 4 K is also included in Figure 2b, for comparison. The temperature-dependent Raman spectra of ZrS$_2$, ZrSSe, and ZrSe$_2$ are shown in Figure S3. The in-plane ($E_g$) and out-plane ($A_{1g}$) Raman modes can be detected in these ZrX$_2$ related layer crystals. At 300 K, ZrS$_{2-x}$Se$_x$ ($x = 0, 1,$ and 2) exhibit much broadened peaks compared to those measured at 4 K owing to thermal effect on lattice vibration. An $A_{2u}$ (LO) peak near $A_{1g}$ of ZrS$_2$ is detected which may be caused by IR mode [32] or by non-harmonic effect of $A_{1g}$ induced by acoustic phonon [33]. Figure 2c shows the representative scheme of vibrated eigen-modes of ZrX$_2$ [32]. ZrS$_2$ reveals three peaks positioned at 246 ± 2 ($E_g$), 316 ± 2 ($A_{2u}$) and 332 ± 2 cm$^{-1}$ ($A_{1g}$), as well as IR mode $2E_u$ at approximately 680 ± 2 cm$^{-1}$ at 300 K. Raman spectrum of ZrSSe reveals strong $A_{1g}$ mode at ~214 cm$^{-1}$ and weak $E_g$ mode at 133 ± 2 cm$^{-1}$. The longitudinal optical mode $E_u$ appears at 286 ± 2 cm$^{-1}$. For ZrSe$_2$, there are three peaks positioned at 126 ± 2 ($E_g$), 191 ± 2 ($A_{1g}$), and 262 ± 2 cm$^{-1}$ ($E_u$) at 300 K. The Raman modes of the ZrS$_{2-x}$Se$_x$ ($x = 0, 1,$ and 2) series show frequency-reduction behavior with the increase of Se content. The heavier selenium atom causes the vibration peak shifted to lower wavenumber for identification of Se doping effect. Figure 2d shows the Raman shift of $A_{1g}$ mode as a function of temperature from 4 to 300 K. The variation mode follows a linear dependence of intensity with temperature in ZrS$_{2-x}$Se$_x$ ($x = 0, 1,$ and 2).

Figure 2. Raman spectra of ZrS$_{2-x}$Se$_x$ ($x = 0, 1,$ and 2) at (a) 300 K and (b) 4 K. (c) The illustration of atomic movements of vibrational modes. (d) Raman frequency of $A_{1g}$ mode as a function of temperature in ZrS$_{2-x}$Se$_x$ ($x = 0, 1,$ and 2).
3.3. Optical Band Gap and Valence-Band Structure

To further characterize the ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2) series, transmittance measurement and X-ray photoelectron spectroscopy (XPS) are carried out. The transmittance measurement is very useful to evaluate optical absorption near band-edge portion \[35\]. The transmittance spectrum needs to be measured at near-normal incidence, and the absorption coefficient should be determined from measured transmittance by examining the spectral dependence of reflectance \[35\]. The transmittance spectra of ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2) crystals measured at 300 K were shown in Figure 3a. The thickness of the crystal was controlled to be ~6 \(\mu\)m to ~10 \(\mu\)m measured by atomic force microscopy. Essentially, bulk ZrX\(_2\) series crystals were mechanically exfoliated to \(\mu\)m scale to obtain fresh surface using Scotch tape. It is noticed that even a little oxide (ZrO\(_2\)) still existed on the surface of ZrS\(_2\); the band gap of ZrO\(_2\) (~5 eV) is usually larger than ZrS\(_2\), similar to that of Ga\(_2\)O\(_3\) \[36\] > Ga\(_2\)S\(_3\) \[37\] and In\(_2\)O\(_3\) \[38\] > In\(_2\)S\(_3\) \[39\]. There is no light-shielding effect from the surface oxide on ZrX\(_2\) when doing transmittance.

The related band-edge value of ZrX\(_2\) could be obtained by analyzing the photon (E\(_g\)) and phonon (E\(_p\)) energies expressed by \(a(h\nu) = (h\nu - E_g + E_p)^2/[\exp(E_p/kT) - 1] + (h\nu - E_g - E_p)^2/[1 - \exp(-E_p/kT)]\) for assisting an indirect transition of absorption and emission of a phonon in the optical process. The plot of \((a(h\nu)^{1/2}\) versus \(h\nu\) for the analysis of indirect gaps are shown in Figure 3b. The indirect band edge E\(_g\) of each crystal is 1.78 eV for ZrS\(_2\), 1.32 eV for ZrSSe, and 1.12 eV for ZrSe\(_2\) at 300 K. These values are in agreement with previous result reported for ZrS\(_2\) and ZrSSe \[40\]. The obtained phonon energies from the linear fits of \((a(h\nu)^{1/2}\) versus \(h\nu\) \[41\] are E\(_p\) = 40 ± 10 meV for all the ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2) series. The variation of indirect band edge indicated the doping effect of selenium content in pure ZrS\(_2\) would cause the band-edge position shifting to lower energy with increasing Se content. This situation resembled the gradual lattice constant change with respect to the increasing of selenium composition obtained by XRD and HRTEM measurements. The XPS spectra in Figure 3c show the main valence-band structure of ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2 with fresh surface) is coming from Zr 4\(d\) hybrid with chalcogen \(p\) orbital. According to the electron configuration, transition metal Zr \(d\) electrons used to have bonding with chalcogen S/Se, which forms Zr\(^{4+}\) (\(d^0\)\(s^0\)) configuration connected to 2(S/Se)\(^2-\) (\(s^2p^6\)) \[42\]. For octahedral coordination, the \(d\) orbitals will split into two sets of energies due to the trigonal distortion and ligand field. The higher energy set comes from \(d_z^2\) symmetry and lower energy set comes from \(d_{xy}, d_{xz}, d_{yz}\) symmetry \[43\]. For group IVB TMDC materials, especially for the ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2) series, the \(d_z^2\) set is vacant and forms the lowest conduction band. The complete set of XPS spectra were also measured and displayed in Figure S4 for comparison. The energies of Zr \(3d\), S \(2p\), and Se \(3d\) orbitals show redshift as the Se content is increased in the ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2) series. It also verifies a little oxygen-incorporation effect in the ZrS\(_{2-x}\)Se\(_x\) (x = 0, 1, and 2) series layer crystals.
Essentially, bulk ZrX$_2$ series crystals were mechanically exfoliated to µm scale to obtain fresh surface. Crystals of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) were prepared. Because the existence of defects, surface states, surface oxide (i.e., ZrX$_2$O$_n$, x = 0 to 2), etc., room-temperature resistivity and Hall-effect measurements of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) were also done to identify their electrical property. The results are listed in Table S2, for comparison. The carrier type of all the ZrX$_2$ series was n type, and carrier concentrations were determined to be 4.05 × 10$^{17}$ cm$^{-3}$ for ZrS$_2$, 1.6 × 10$^{18}$ cm$^{-3}$ for ZrSSe, and 2.9 × 10$^{18}$ cm$^{-3}$ for ZrSe$_2$, respectively. The high carrier concentration also renders lower resistivity of 0.25 Ω-cm for ZrS$_2$, 0.0211 Ω-cm for ZrSSe, and 0.0058 Ω-cm for ZrSe$_2$, respectively. Figure 4a shows temperature dependent resistivity of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series as a function of reciprocal temperature. The series shows metallic carrier-conduction behavior due to the increasing resistivity as the temperature increased. The lower resistivity of the ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series may come from heavily doping from defects, like chalcogen vacancies or native impurities, i.e., surface oxidation states in air (or from environment water vapor) [46], which cause the material to behave like a degenerate semiconductor, as the band scheme shown in the inset of Figure 4d. Dissimilar to the other 2D materials, like MoS$_2$ and MoSe$_2$, ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series exhibits relatively low resistivity owing to the surface states. The sign of Seebeck coefficient (S = −ΔV/ΔT) indicates all three ZrX$_2$ compounds are n-type semiconductor as shown in Figure 4b. The carrier type is similar to that determined by Hall-effect measurements.

3.4. Transport and Thermoelectric Properties

For the characterization of electrical and thermoelectric properties of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series layer crystals, temperature-dependent resistivity and thermoelectric measurements from 20 to 300 K were carried out. Since many researchers have claimed that ZrX$_2$ (X = S, Se) series displayed good thermoelectric properties, we measured the experimental result and compared with previous theoretical results [44,45] herein. The layered samples of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) crystals with dimension about 0.45 × 0.12 × 0.01 cm$^3$ were prepared. Because the existence of defects, surface states, surface oxide (i.e., ZrX$_2$O$_n$, x = 0 to 2), etc., room-temperature resistivity and Hall-effect measurements of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) were also done to identify their electrical property. The results are listed in Table S2, for comparison. The carrier type of all the ZrX$_2$ series was n type, and carrier concentrations were determined to be 4.05 × 10$^{17}$ cm$^{-3}$ for ZrS$_2$, 1.6 × 10$^{18}$ cm$^{-3}$ for ZrSSe, and 2.9 × 10$^{18}$ cm$^{-3}$ for ZrSe$_2$, respectively. The high carrier concentration also renders lower resistivity of 0.25 Ω-cm for ZrS$_2$, 0.0211 Ω-cm for ZrSSe, and 0.0058 Ω-cm for ZrSe$_2$, respectively. Figure 4a shows temperature dependent resistivity of ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series as a function of reciprocal temperature. The series shows metallic carrier-conduction behavior due to the increasing resistivity as the temperature increased. The lower resistivity of the ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series may come from heavily doping from defects, like chalcogen vacancies or native impurities, i.e., surface oxidation states in air (or from environment water vapor) [46], which cause the material to behave like a degenerate semiconductor, as the band scheme shown in the inset of Figure 4d. Dissimilar to the other 2D materials, like MoS$_2$ and MoSe$_2$, ZrS$_{2-x}$Se$_x$ (x = 0, 1, and 2) series exhibits relatively low resistivity owing to the surface states. The sign of Seebeck coefficient (S = −ΔV/ΔT) indicates all three ZrX$_2$ compounds are n-type semiconductor as shown in Figure 4b. The carrier type is similar to that determined by Hall-effect measurements.
The concentration value was claimed to be an optimum carrier density for achieving optimal ZT in ZrS2 crystals [50]. ZrSe, ZrS, and electron concentration are also increased to promote thermoelectric performance in the ZrSe2 compound [48,49]. Figure 4d shows the ZT values of the ZrS2−xSex (x = 0, 1, and 2) series from 20 to 300 K. The ZT values of all samples increase when the temperature is increased, while thermal conductivity κ decreases when the temperature is raised (see Figure 4c). At 300 K, the highest ZT value of 0.085 was achieved by ZrSe2, followed by ZrS0.5Se1.5 of ZT = 0.06 and ZrS2 of ZT = 0.02, respectively. When the Se content increases, the mobility and electron concentration are also increased to promote thermoelectric performance in the ZrS2−xSex (x = 0, 1, and 2) series. The carrier concentration of ZrSe2 is close to ~10^19 cm⁻³ in Table S2. The concentration value was claimed to be an optimum carrier density for achieving optimal ZT in the thermoelectric materials [50]. ZrSe2 is therefore shows the best thermoelectric performance in the ZrS2−xSex (x = 0, 1, and 2) series layered TMDCs.

![Figure 4](image-url)

**Figure 4.** (a) Resistivity as function of reciprocal temperature. (b) Seebeck coefficient of ZrS2−xSex (x = 0, 1, and 2) as function of temperature. (c) Thermal conductivity as function of temperature of ZrS2−xSex (x = 0, 1, and 2). The inset shows the experimental configuration of thermoelectric measurement. (d) The dependences of ZT values (figure of merit) versus temperature.
4. Conclusions

In conclusion, ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$) crystals were successfully grown by CVT method. The structural, optical, and thermoelectric properties of the compounds were characterized. The HRTEM, SAED, and XRD results confirmed the 1T-CdI$_2$ structure. The ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$) series revealed an indirect band gap positioned at 1.78 eV, 1.32 eV, and 1.12 eV, respectively. The energy gap varies accordingly with Se composition change, which indicates the similar electronic and band structures of the layered ZrX$_2$ ($X = S, \text{Se}$). A few layers of Raman spectra of ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$) were observed from 4 to 300 K. The frequencies of vibration modes decreased with the increase of Se content due to the heavier atomic weight of Se. All the layered ZrS$_{2-x}$Se$_x$ reveal chalcogen deficiency and existing native oxide (ZrX$_{2-x}$O$_x$) and surface states on its surface to render lower resistivity compared to the other 2D wide-gap TMDCs. Temperature-dependent resistivity shows degenerate semiconductor behavior of all ZrS$_{2-x}$Se$_x$ layer compounds, with ZrSe$_2$ possessing the lowest resistivity. Along with Hall-effect measurement, ZrSe$_2$ also shows higher mobility and higher electron concentration to promote carrier transport and thermoelectric performance in the layered ZrS$_{2-x}$Se$_x$. At 300 K, the ZT is increased, and κ is decreased, with the increase of the Se content. An experimental value of $ZT \approx 0.085$ is obtained for ZrSe$_2$ owing its enhanced mobility and optimal carrier concentration in the ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$) series layered crystals.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/4/327/s1, Figure S1: Crystal morphology of $c$-plane layered ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Figure S2: Energy Dispersive X-ray (EDX) analysis of ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Figure S3: Temperature-dependent Raman spectra of ZrS$_2$, ZrSe$_2$, and ZrSSe. Figure S4: The XPS spectra of (a) Zr 3d$_{3/2}$ and Zr 3d$_{5/2}$, (b) S 2p$_{3/2}$ and S 2p$_{1/2}$, and (c) Se 3d$_{5/2}$ and Se 3d$_{3/2}$ in ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Table S1: The comparison of lattice constants of ZrS$_{2-x}$Se$_x$ obtained by XRD and TEM measurements. Table S2: Resistivity and Hall measurement results at 300 K.

Author Contributions: T.M.H. and C.-H.H. synthesized the compounds and grew the crystals. C.-H.H. conceives (EDX) analysis of ZrS$_2$, (b) S 2p$_{3/2}$ and S 2p$_{1/2}$, and (c) Se 3d$_{5/2}$ and Se 3d$_{3/2}$ in ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Table S1: The comparison of lattice constants of ZrS$_{2-x}$Se$_x$ obtained by XRD and TEM measurements. Table S2: Resistivity and Hall measurement results at 300 K. Figure S1: Crystal morphology of $c$-plane layered ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Figure S2: Energy Dispersive X-ray (EDX) analysis of ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Figure S3: Temperature-dependent Raman spectra of ZrS$_2$, ZrSe$_2$, and ZrSSe. Figure S4: The XPS spectra of (a) Zr 3d$_{3/2}$ and Zr 3d$_{5/2}$, (b) S 2p$_{3/2}$ and S 2p$_{1/2}$, and (c) Se 3d$_{5/2}$ and Se 3d$_{3/2}$ in ZrS$_{2-x}$Se$_x$ ($x = 0, 1, \text{and} 2$). Table S1: The comparison of lattice constants of ZrS$_{2-x}$Se$_x$ obtained by XRD and TEM measurements. Table S2: Resistivity and Hall measurement results at 300 K.

Author Contributions: T.M.H. and C.-H.H. synthesized the compounds and grew the crystals. C.-H.H. conceives the research idea and designs & implements the thermoelectric-measurement system. T.M.H. did the optical and electrical measurements under the supervision of C.-H.H.; T.M.H. and C.-H.H. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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