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Research Article

Thermoelectric Properties of a Single Crystalline Ag_2Te Nanowire

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Silver chalcogenides have received much attention in potential thermoelectric materials research because of high carrier mobility and low effective mass. Among them, in Ag_2Te, it was reported that the phase transition from monoclinic to cubic phase occurs at relatively low temperatures, so that extensive research for effective application using this material has been aroused. In this work, we investigated how 1-dimensional nanostructure affects the thermoelectric properties through as-synthesized single crystalline Ag_2Te nanowires. Adopting well-defined thermoelectric MEMS device structure and transferring an individual Ag_2Te nanowire, we measure electrical resistance and Seebeck coefficient as a function of temperature. When the phase changes from monoclinic to cubic, the resistance increases, while absolute Seebeck coefficient value decreases. These results are compared with previous reports for Ag_2Te bulk and film, suggesting the increased density of states of the carriers due to nanowire structure.

1. Introduction

Silver chalcogenides (Ag_2X; X = S, Se, and Te) have attracted much attention due to low effective mass and high carrier mobility [1–3]. Ag_2Te among silver chalcogenides has aroused significant interests in the field of topological insulators field through recent reported quantum phenomena [4–6]. Most thermoelectric materials having topological insulating properties due to strong spin-orbit coupling have been studied for the improvement of thermoelectric properties prior to establishing the concept of topological insulators. Ag_2Te reveals the phase transition from narrow-gap semiconductor to superionic conductor at 130~150°C [7]. In addition, the monoclinic structure of Ag_2Te changes into face-centered cubic and body-centered cubic phase at 145 and 802°C, respectively [8]. Such structural phase transition can induce the modification of electrical transport and lattice volume, closely related to thermoelectric properties.

For the future energy industry, thermoelectric technology, which converts thermal waste to electrical power, plays an indispensable role for efficiently supplying energy that can be lost in devices [9, 10]. The performance of thermoelectric devices is determined by the dimensionless figure of merit (ZT), expressed in $ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, and κ is the total thermal conductivity. κ consists of electron (κ_e) and lattice thermal conductivities (κ_L), respectively. These values strongly depend on the electronic structures and physical parameters of carriers, often adversely affecting each physical parameter [11]. For semiconductors with wide bandgap, the Seebeck coefficient can increase, but the electrical resistivity decreases due to low carrier concentration. Moreover, if metallic materials are used for lower resistivity, thermal conductivity increases because temperature difference between end sides of the materials is similar. However, when downsizing as the nanoscale, the thermal conductivity is significantly reduced owing to smaller dimensions than the mean free path of the phonons and enhancement of density of states via quantum confinement effect [12–14]. Several research groups have focused on the low-dimensional systems of well-known thermoelectric materials for improvement of the performance like increasing ZT.

In this work, we investigated the thermoelectric properties of an individual Ag_2Se nanowire around phase transition temperature. High quality single crystalline Ag_2Te nanowires are synthesized by simple chemical vapor transport method.

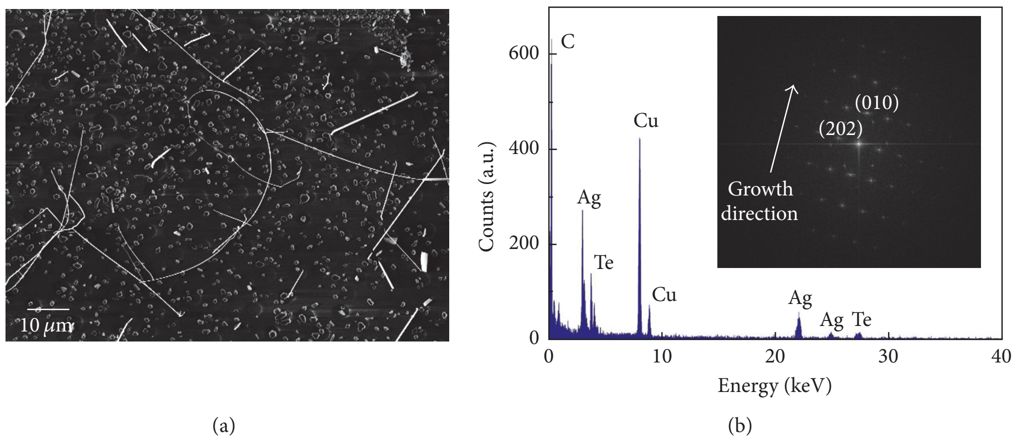


Figure 1: (a) SEM image of as-grown Ag_2Te nanowires on a sapphire substrate. (b) TEM-EDS spectrum of single Ag_2Te nanowire. C and Cu peaks are originated from a TEM grid. Inset: FFT of lattice resolved TEM image, indicating high quality single crystalline nature and (010) growth direction.

By a home-made nanomanipulator, individual nanowire is transferred to prepatterned microelectromechanical systems (MEMS) membrane. Applying the current into nanoheater electrodes, we observe drastic changes of both resistance and Seebeck coefficient around phase transition temperature (130°C).

2. Materials and Methods

Single crystalline Ag_2Te nanowires were synthesized in a horizontal one-zone furnace with a 1-inch diameter quartz tube. Ag_2Te powder was used as the starting precursor in the synthesis of Ag_2Te nanowires. Sapphire (α-Al_2O_3) substrates were placed at ~12 cm from the boat containing the precursors. Prior to loading the quartz tube was degassed and purged with high purity argon gas, supplied with a flowrate of 30 standard cubic centimeters per minute (sccm) under 10 Torr. The furnace was set to 980°C for 30 minutes with 40°C/min ramping rate. Morphology and structural analyses of the grown Ag_2Te nanowires were performed using a combination of scanning electron microscope (SEM) and transmission electron microscope (TEM).

Thermoelectric measurement was carried out using a membrane-type microdevice, which was fabricated on Si wafer coated with 500 nm thick SiN layer by e-beam lithography technique. A microelectrode pattern, which consists of a symmetric pair of Pt nanoheater electrodes, Pt thermometers, and current carrying electrodes, was defined in the center of the microdevice using a UV stepper. The microelectrode was formed by e-beam evaporation (Pt/Ti = 40 nm/10 nm). The backside Si beneath the micropattern was etched away in a KOH solution so that the microdevice has a SiN membrane structure to enhance the measurement sensitivity. An individual Ag_2Te nanowire was transferred from the sapphire substrate to the microdevice using a nanomanipulator. We adopted sputter deposition of Pt/Ti = 90 nm/5 nm to make electrical and thermal contacts between the electrodes and the sample.

3. Results and Discussion

The SEM image of Figure 1(a) shows as-grown Ag_2Te nanostructures including nanowires and nanoplates on a sapphire substrate. In spite of low density, Ag_2Te nanowires are several tens of micrometers long and 100 to 200 nm in diameter. For Ag_2Te nanoplates, the geometry with approximate 3 μm width and 10 μm length is observed.

The elemental composition of as-synthesized Ag_2Te nanowires was examined by energy dispersive X-ray spectrometry (EDS) using TEM. Figure 1(b) reveals the TEM-EDS spectrum taken from a single Ag_2Te nanowire. The atomic ratio of Ag and Te elements is approximately 2 : 1 within an instrumental accuracy, confirming that the nanowire is composed of only Ag and Te. Except C and Cu from the TEM grid, no impurities and metal catalyst are observed. As shown in the inset of Figure 1(b), the two-dimensional fast Fourier transform (FFT) of the lattice resolved image obtained from the TEM shows a regular spot pattern, indicating high quality single crystalline nature. Furthermore, the spots pattern can be fully indexed to the monoclinic Ag_2Te phase via lattice spacing and demonstrate that the nanowire growth is along the [010] direction down the [100] zone axis. All the structural and compositional results are consistent with prior reports [6].

Figure 2 shows the representative SEM image of thermoelectric device and single Ag_2Te nanowire that we used for our experiments. To prevent heat from diffusing out to the Si substrate, the device platform is suspended. The electrical resistance of the Ag_2Te nanowire is measured by 4-probe method. In addition, the thermal gradient across the nanowire is detected by 4-point thermometry electrodes. During thermal expansion, Ag_2Te nanowire is clamped on the electrode using Pt, avoiding the change in the contact area caused by the movement of the nanowire (inset of Figure 2).

In Seebeck coefficient measurement, Pt nanoheater electrodes are used to generate a temperature gradient ΔT across

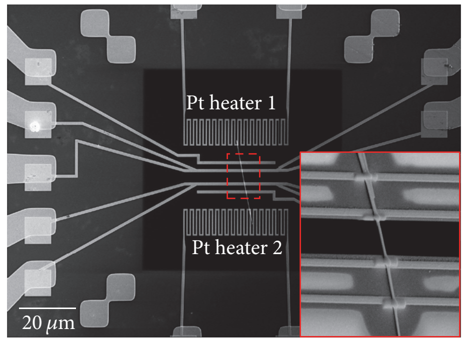
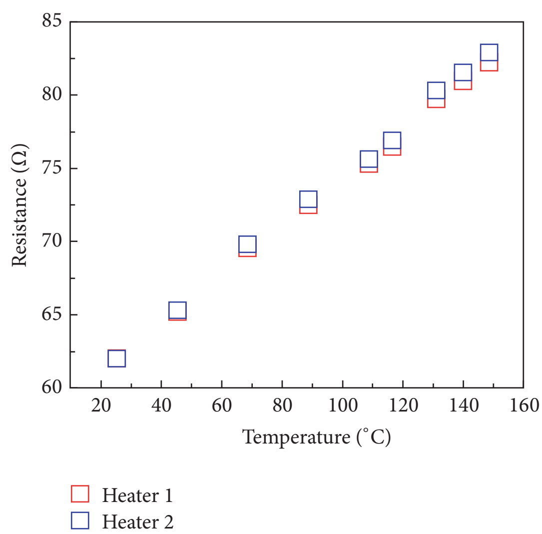
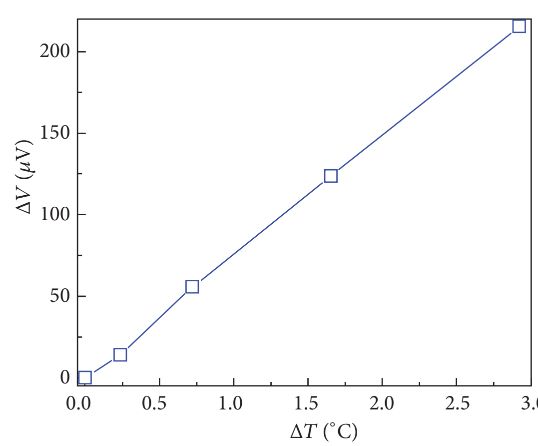


FIGURE 2: SEM image of thermoelectric MEMS structure with Ag_2Te nanowire. Inset: magnified SEM image of the red square box in the main Figure 2.



(a)



(b)

FIGURE 3: (a) Resistance of Pt nanoheaters 1 and 2. The resistance values of each nanoheater are converted into temperatures at hot and cold sides. (b) Thermoelectric voltage (ΔV) as a function of temperature gradient (ΔT) across the sample.

the sample. The thermoelectric voltage ΔV in the sample is measured using a nanovoltmeter. The temperature difference ΔT between the hot and cold sides is determined by the change of resistance at the Pt thermometers using lock-in amplifiers. To convert the resistance change into ΔT, the temperature coefficients of resistance (TCR) of the Pt thermometers are estimated for each of samples. By linear fitting of the resistance as a function of the temperature, the TCR is typically calculated to be about 0.1636 $\Omega/^{\circ}$C as seen in Figure 3(a). ΔV is measured at different heater powers, leading to the Seebeck coefficient taken from a linear fitting of the $\Delta V/\Delta T$ plot in Figure 3(b). Indeed, a switching module (scanner relay) is adopted to make the Pt thermometers play the dual roles of a thermometer and a voltage probe without signal interference: two lock-in amplifiers read ΔT in the relay-on state while the nanovoltmeter measures ΔV in the relay-off state.

Figure 4 shows current-voltage (I-V) curves of Ag_2Te nanowire measured by 4-probe method at various temperatures, exhibiting ohmic behavior. The resistance of Ag_2Te nanowire at 120°C is about 6.43 kΩ. When the temperature of the thermal heater membranes increases over 130°C, the resistance of Ag_2Te nanowire suddenly increases to be about 27.35 kΩ. As shown in the inset of Figure 4, the resistance at the temperatures over 130°C slightly decreases with increasing temperature, owing to larger band gap in the cubic phase.

Figure 5 shows the Seebeck coefficient as a function of the temperature measured from Ag_2Te nanowire. As previous studies reported that Ag_2Te is n-type semiconductor [1, 6, 15], the Seebeck coefficient reveals negative values, confirming that the majority of charge carriers are electrons. The Seebeck coefficients also drastically change at 130°C, similar trend of the resistance. Such results indicate that there is a phase transition of Ag_2Te nanowires between 120°C and 130°C, consistent with reported results [16–18]. The Seebeck coefficient is strongly related to the carrier density. In general, the absolute Seebeck coefficient values increase with decreasing carrier density in semiconductors [19], similar with previous reports in Ag_2Te pellets and Ag_2Te film [17, 18].

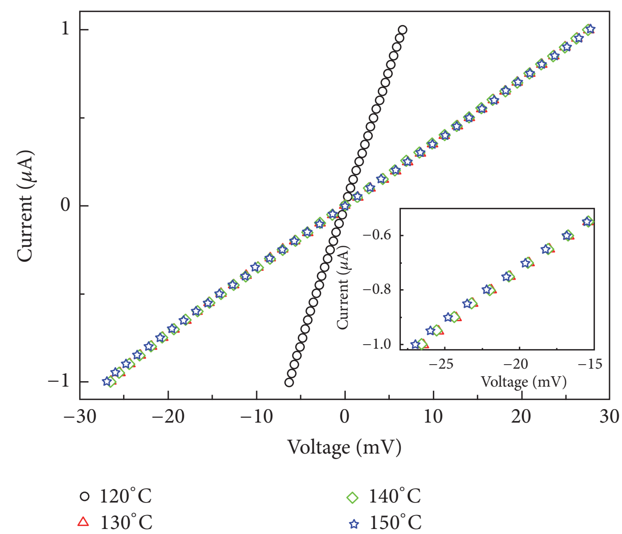


FIGURE 4: *I-V* characteristics of individual Ag_2Te nanowire measured at various temperatures. Inset: enlarged *I-V* curves ranged from −1.0 μA to −0.5 μA.

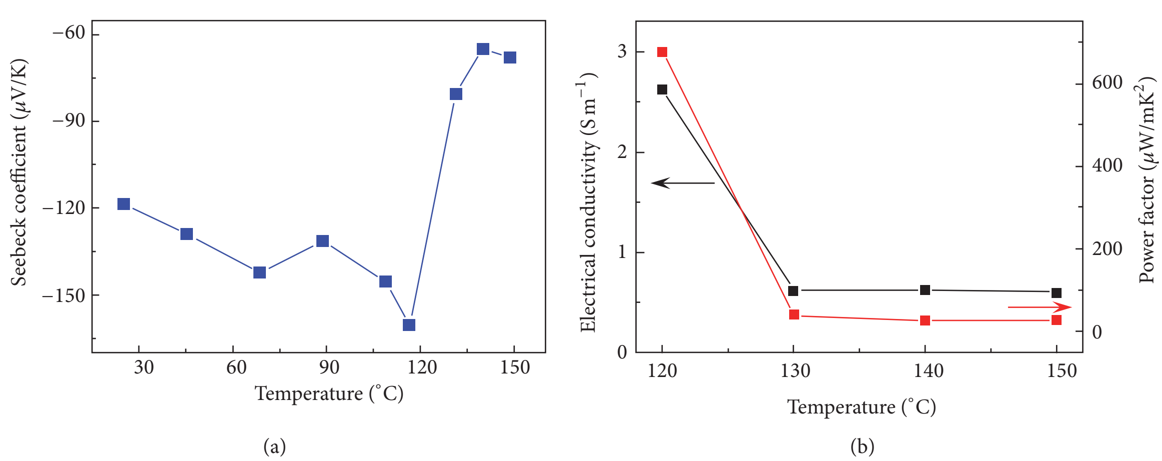


FIGURE 5: (a) Temperature dependent Seebeck coefficient of Ag_2Te nanowire. (b) Electrical conductivity and power factor of the same Ag_2Te nanowire.

However, our results for the single Ag_2Te nanowire show that, with increasing temperature, the absolute Seebeck coefficient values slightly decrease followed by sudden increment before phase transition, but electrical conductivity simultaneously decreases in cubic phase regime as shown in Figure 5(b). Such opposite feature may stem from increased density of states of the electrons when the structural dimension is reduced like nanowires. Figure 5(b) shows the thermopower factor, $S^2\sigma$, where S and σ are Seebeck coefficient and electrical conductivity, respectively. When the phase of Ag_2Te changes into cubic, power factor suddenly decreases up to 25 μW/mK^2, but larger value than other polycrystalline Ag_2Te results [20, 21]. Our Ag_2Te nanowires with single crystalline nature grown by vapor-solid method result in the benefit to higher electrical conductivity, expecting excellent performance like high *ZT* for thermoelectric applications.

4. Conclusions

We have successfully synthesized high quality single crystalline Ag_2Te nanowires by simple chemical vapor deposition. Adopting the fabrication of MEMS device for measuring thermoelectric properties and transferring individual Ag_2Te nanowire, we observe the temperature dependent resistance and Seebeck coefficient, where the resistance and absolute Seebeck coefficient decrease with increasing temperature over phase transition temperature, different trend from other dimensional Ag_2Te structures. These results pave the way to explore not only the thermoelectric properties of silver chalcogenide topological insulators, but also the potential application for the efficient thermoelectric devices using nanostructures.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

[1] V. D. Das and D. Karunakaran, "Thermoelectric studies on semiconducting Ag_2Te thin films: temperature and dimensional effects," *Physical Review B*, vol. 30, no. 4, pp. 2036–2041, 1984.

[2] C. Xiao, J. Xu, K. Li, J. Feng, J. Yang, and Y. Xie, "Superionic phase transition in silver chalcogenide nanocrystals realizing optimized thermoelectric performance," *Journal of the American Chemical Society*, vol. 134, no. 9, pp. 4287–4293, 2012.

[3] V. Krylova and N. Dukštienė, "Synthesis and characterization of Ag_2S layers formed on polypropylene," *Journal of Chemistry*, vol. 2013, Article ID 987879, 11 pages, 2013.

[4] R. Xu, A. Husmann, T. F. Rosenbaum, M.-L. Saboungi, J. E. Enderby, and P. B. Littlewood, "Large magnetoresistance in non-magnetic silver chalcogenides," *Nature*, vol. 390, no. 6655, pp. 57–60, 1997.

[5] W. Zhang, R. Yu, W. Feng et al., "Topological aspect and quantum magnetoresistance of β-Ag_2Te," *Physical Review Letters*, vol. 106, no. 15, Article ID 156808, 2011.

[6] S. Lee, J. In, Y. Yoo et al., "Single crystalline β-Ag_2Te nanowire as a new topological insulator," *Nano Letters*, vol. 12, no. 8, pp. 4194–4199, 2012.

[7] A. Qin, Y. Fang, P. Tao, J. Zhang, and C. Su, "Silver telluride nanotubes prepared by the hydrothermal method," *Inorganic Chemistry*, vol. 46, no. 18, pp. 7403–7409, 2007.

[8] J. In, Y. Yoo, J.-G. Kim et al., "In situ TEM observation of heterogeneous phase transition of a constrained single-crystalline Ag_2Te nanowire," *Nano Letters*, vol. 10, no. 11, pp. 4501–4504, 2010.

[9] L.-D. Zhao, S.-H. Lo, Y. Zhang et al., "Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals," *Nature*, vol. 508, no. 7496, pp. 373–377, 2014.

[10] S. H. Park, S. Jo, B. Kwon et al., "High-performance shape-engineerable thermoelectric painting," *Nature Communications*, vol. 7, Article ID 13403, 2016.

[11] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, "Thin-film thermoelectric devices with high room-temperature figures of merit," *Nature*, vol. 413, no. 6856, pp. 597–602, 2001.

[12] A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard III, and J. R. Heath, "Silicon nanowires as efficient thermoelectric materials," *Nature*, vol. 451, no. 7175, pp. 168–171, 2008.

[13] A. Boukai, K. Xu, and J. R. Heath, "Size-dependent transport and thermoelectric properties of individual polycrystalline bismuth nanowires," *Advanced Materials*, vol. 18, no. 7, pp. 864–869, 2006.

[14] J. R. Szczech, J. M. Higgins, and S. Jin, "Enhancement of the thermoelectric properties in nanoscale and nanostructured materials," *Journal of Materials Chemistry*, vol. 21, no. 12, pp. 4037–4055, 2011.

[15] A. Sulaev, W. Zhu, K. L. Teo, and L. Wang, "Gate-tuned quantum oscillations of topological surface states in β-Ag2Te," *Scientific Reports*, vol. 5, Article ID 8062, 2015.

[16] P. Gnanadurai, N. Soundararajan, and C. E. Sooriamoorthi, "Studies on the electrical conduction in silver telluride thin films," *Physica Status Solidi (B) Basic Research*, vol. 237, no. 2, pp. 472–478, 2003.

[17] F. Li, C. Hu, Y. Xiong, B. Wan, W. Yan, and M. Zhang, "Phase-transition-dependent conductivity and thermoelectric property of silver telluride nanowires," *Journal of Physical Chemistry C*, vol. 112, no. 41, pp. 16130–16133, 2008.

[18] D.-Y. Jung, K. Kurosaki, Y. Ohishi, H. Muta, and S. Yamanaka, "Effect of phase transition on the thermoelectric properties of Ag_2Te," *Materials Transactions*, vol. 53, no. 7, pp. 1216–1219, 2012.

[19] K. Park, K. U. Jang, H.-C. Kwon, J.-G. Kim, and W.-S. Cho, "Influence of partial substitution of Cu for Co on the thermoelectric properties of $NaCo_2O_4$," *Journal of Alloys and Compounds*, vol. 419, no. 1-2, pp. 213–219, 2006.

[20] H. Yang, J.-H. Bahk, T. Day et al., "Composition modulation of Ag_2Te nanowires for tunable electrical and thermal properties," *Nano Letters*, vol. 14, no. 9, pp. 5398–5404, 2014.

[21] H. Zhu, J. Luo, H. Zhao, and J. Liang, "Enhanced thermoelectric properties of p-type Ag_2Te by Cu substitution," *Journal of Materials Chemistry A*, vol. 3, no. 19, pp. 10303–10308, 2015.