New methods for enhancing $ZT$ value of nanowires

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Abstract. We report an important modulating factor, degeneracy, for $ZT$ value enhancement of nanowire. Three approaches to design nanowire of large $ZT$ value by degeneracy effects are proposed: (1) controlling growth direction, (2) increasing the number of near degenerate conduction (valence) subbands induced by quantum confinement and (3) searching for bulk materials with two (or more) sets of near degenerate conduction (or valence) bands to fabricate nanowires.

1. Introduction
Thermoelectricity is one of the simplest technologies applicable to energy conversion. The efficiency of thermoelectricity is governed by a basic property of thermoelectrical material, dimensionless figure of merit $ZT = \frac{S^2 \sigma}{\kappa T}$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity which consists of electron and lattice thermal conductivity, $\kappa_e$ and $\kappa_L$, and $T$ is the absolute temperature. In the 1990’s Hicks and Dresselhaus pointed out that low dimensional materials should have better efficiency than bulk ones due to low-dimensional effects on both charge carriers and lattice waves\cite{1,2}. The validity of attaining higher $ZT$ value in low dimension systems has been experimentally demonstrated on Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices \cite{3} and on PbTe/PbSeTe quantum-dots \cite{4} with $ZT \sim 2.4$ and 1.6 respectively at 300K.

Therefore, nanowires are potentially good thermoelectrical systems for application. In this paper, we report another important modulating factor in $ZT$ value enhancement of nanowire, degeneracy. Three approaches to design nanowire of large $ZT$ value by degeneracy effects are proposed. The degeneracy effects on $ZT$ value enhancement of nanowire are demonstrated by the calculated $ZT$ values of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ wires with diameter below 10 nm along trigonal and binary axes.

2. Theoretical approaches
The band structure and the thermoelectric transport properties of nanowires are calculated via the theoretical approach from Ref.\cite{5}. In such an approach, the cylindrical wire boundary conditions, the anisotropic carrier effective mass tensor and the multiple carrier pockets are taken into account to calculate the band structure, and the thermoelectric transport coefficients are obtained from a semiclassical model based on the Boltzmann transport equation. The effective mass parameters are from Refs.\cite{6,7} and the parameters for calculating thermoelectric transport properties are from Refs.\cite{1,8,9,10,11,12,13,14}.
3. Results and discussions
The obtained $ZT$ value at 300 K as a function of Fermi energy for Bi$_2$Te$_3$ (n-type and p-type) and Sb$_2$Te$_3$ (p-type) nanowires with different diameters (10 nm and 5 nm) are presented in Fig. 1 and Fig. 2. The nanowires are orientated along the two principal crystallographic axes (trigonal and binary directions). Zero energy level is selected at the center of band gap of bulk material for Bi$_2$Te$_3$ wire and valence band edge of bulk material for Sb$_2$Te$_3$ wire, respectively. The lowest subband edge of electrons is labeled by $\varepsilon_e^{(0)}$ and the highest one of holes is denoted by $\varepsilon_h^{(0)}$. As shown in the two figures, the $ZT$ values are quite small for the nanowires with a diameter of 10 nm when only one subband is taken into account, due to low mobility of carriers in Bi$_2$Te$_3$ and Sb$_2$Te$_3$. As the diameter reduces, $ZT$ value increases significantly owing to the quantum confinement. However, the increment ratio is not so large as in Bi nanowire [5] since the thermal conductivity is affected little by this quantum effect for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ wires. Another general feature is that all the Fermi energies are near the subband edges but not exactly at these points when largest $ZT$ values occur. Comparatively, we find that, for Bi$_2$Te$_3$, n-type wire may be more favorable in application than p-type owing to the relatively larger mobility and smaller effective mass. We also notice that the maximal $ZT$ value of Sb$_2$Te$_3$ wire are smaller than that of Bi$_2$Te$_3$ wire with the same reasons.

Now we look into the importance of degeneracy. For bulk Bi$_2$Te$_3$ and Sb$_2$Te$_3$ materials, most attentions have been paid to the cleavage plane in that the mobility in this plane is much higher than that along trigonal direction. However, when such materials are fabricated as thin nanowires, the trigonal direction becomes important. As demonstrated in Fig. 1, the maximal $ZT$ values of trigonal wires are larger than those of binary wires even though the mobility in binary axis is the highest. We attribute this to degeneracy. Due to the structural difference between nanowire and bulk material, the degeneracy of carrier pocket varies significantly when a wire is orientated along different direction. For a trigonal nanowire made from Bi$_2$Te$_3$ or Sb$_2$Te$_3$, the electron and hole pockets are six-fold degenerate. However, for wires orientated along the binary axis, the carrier pockets are divided into two groups: one denoted as binary group I is four-fold degenerate and another denoted as binary group II is two-fold degenerate. From our results, the lowest conduction (uppermost valence) subband of binary nanowire originates from carrier pockets of binary group II. Therefore, the degeneracy of lowest conduction (uppermost
Figure 2. The Fermi energy dependence of calculated $ZT$ value at 300K for 5nm (a) and 10 nm (b) Sb$_2$Te$_3$ nanowires orientated along binary axis. Energies are respected to the valence band edge of bulk material. $\varepsilon_h^{(0)}$ denotes the highest subband energy edge of holes.

valence) subband of binary nanowire is only one third of that of trigonal wire. Such a difference of degeneracy results in the maximal $ZT$ values of trigonal wires being larger than those of binary wires with small diameter (bellow 10 nm for Bi$_2$Te$_3$). This phenomena can also be found in the theoretical results for Bi nanowire [5]. As a result, we infer that the degeneracy is important in nanowires and favorable thermoelectrical properties can be achieved through controlling the wire direction.

The second interesting phenomenon is exhibited in Fig. 2 which shows the calculated $ZT$ values as a function of Fermi level for Sb$_2$Te$_3$ nanowires with diameter 10 nm and 5 nm in binary direction. We find a significant enhancement of $ZT$ value comparing the multi-subband contribution (dashed line in Fig. 2(a)) with single subband contribution(solid line in Fig.2(a)). This phenomenon can also be found in Bi$_2$Te$_3$ wire orientated along binary axis (see Fig. 1). Moreover, it is very interesting that even the maximum of $ZT$ value for a 10 nm Sb$_2$Te$_3$ wire is larger than that for a 5 nm wire (see Fig. 2(b)). Such a phenomenon originates from another degeneracy effect. For a binary Sb$_2$Te$_3$ nanowire with a diameter of 10 nm, our results show that the edges of first three subbands of binary group II (30.14, 45.95, 66.89 meV) and the first subband of binary group I (65.97 meV) are very vicinal. Hence each of these subbands makes a contribution to the $ZT$ value. If we define vicinal degeneracy as the number of subbands whose energy edges are within 40 meV above (below) the lowest conduction (upermost valence) subband, a vicinal degeneracy with a value of 10 is obtained since the subband of binary II group is two-fold degenerate and the subband of binary group I is four-fold degenerate. However, the vicinal degeneracy decreases when a wire becomes slimmer due to the quantum confinement effect. This is the reason of that 10 nm Sb$_2$Te$_3$ wire has a larger maximal $ZT$ value than 5 nm wire. This vicinal degeneracy effect provides an useful guidance and an easy way to design new favorable thermoelectrical materials since it does not need to fabricate quite slim wire for a large $ZT$ value. Moreover, at a larger diameter, the electrical conductivity is not reduced strongly by localized effect.

The other way to achieve large $ZT$ value through degeneracy effect is searching for (or designing) materials whose bulk band structure has the shape as sketched in Fig. 3. Materials of this type have two conduction (or valence) bands and the difference between the two energy edges is quit small. Moreover, the effective mass of upper conduction (lower valence) band is larger than that of the lower conduction (upper valence) band. For nanowires made from such materials, the energy shifts of the subband edges with respect to the upper bulk conduction (lower valence) band increases more slowly, compared with these respect to the lower conduction(upper valence) band. So, at some critical diameter, some subbands induced from upper bulk conduction (lower valence) band will be close to those induced from lower conduction(upper valence) band. If each subband is multi-fold degenerate, larger vicinal degeneracy can easily been obtained, and it is possible to enhance $ZT$ value significantly. However, an important condition that mobility of upper conduction (or lower valence) band is not too low should be satisfied. In fact, the band
Figure 3. The schematic diagram of bulk band structure for the favorable thermoelectrical material from which nanowire of large $ZT$ value is made. $u_c$, $l_c$, $u_v$, and $l_v$ denote upper conduction band, lower conduction band, upper valence band and lower valence band, respectively.

structures of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ belong to this type. But, unfortunately, the second conduction (valence) band of bulk material has quite low mobility. If this disadvantage is removed, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ nanowires will be favorable in thermoelectrical application.

4. Conclusions
Enhancement of $ZT$ value of nanowire has the potential to be achieved by the following approaches: (1) controlling growth direction, (2) increasing the number of near degenerate conduction (valence) subbands induced by quantum confinement and (3) searching for bulk materials with two (or more) sets of near degenerate conduction (or valence) bands to fabricate nanowires.

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