

# Quantum Confinement Effects on Thermoelectric Nanowires

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## ABSTRACT

Effective thermoelectric energy conversion devices require high thermoelectric figure of merit, which has approached the limit for bulk materials. Low dimensional systems such as nanowires, however, may have enhanced thermoelectric figure of merit and thus break this limit due to quantum confinement effects and increased phonon boundary scattering. In this paper we review the recent studies of these effects on different thermoelectric nanowires systems.

## INTRODUCTION

The efficiency of thermoelectric energy conversion devices is a function of thermoelectric figure of merit  $ZT$  where  $T$  is the temperature and  $Z$  is defined as  $Z = S^2\sigma/\kappa$  [1]. In the expression of  $Z$ ,  $S$  is Seebeck coefficient,  $\sigma$  is the electrical conductivity and  $\kappa = \kappa_e + \kappa_l$  is the thermal conductivity, which includes contribution from carriers ( $\kappa_e$ ) and from lattice ( $\kappa_l$ ). Large values of  $ZT$  require high  $S$ , high  $\sigma$  and low  $\kappa$ . It is very difficult to increase  $Z$  in bulk thermoelectric materials, because these three material's properties are coupled with each other. Specifically, an increase in  $S$  normally leads to a decrease in  $\sigma$  due to carrier density considerations and an increase in  $\sigma$  implies an increase in the carrier contribution to  $\kappa$  as given by the Wiedemann-Franz law. In fact, the thermoelectric figure of merit  $ZT$  in bulk materials has been approaching the limit; the best bulk thermoelectric materials are alloys of bismuth (Bi) and tellurium (Te) such as  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ , with  $ZT \approx$

1.0 at 300K [2]. It is believed that a  $ZT$  value exceeding 3 is needed in order for a thermoelectric cooler to compete with a vapor compression cooling unit such as a chlorofluorocarbon (CFC)-based refrigerator [3]. Low dimensional materials systems like nanowires may have significantly improved  $ZT$  compared with their bulk counterparts and thus meet this requirement, as shown in a number of theoretical investigations on different nanowire systems [4, 5, 6, 7, 8].

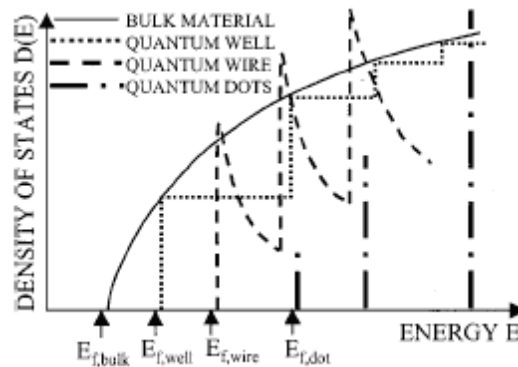


Figure 1. Electronic density of states for 0D quantum dot, 1D quantum wire, 2D quantum well and 3D bulk materials

The possible enhancement in thermoelectric figure of merit  $ZT$  in nanowires stems from quantum confinement effects and increased phonon boundary scattering. As the characterization length of materials is reduced to be comparable with the wavelength of electrons, the motion of carriers (electrons or holes) is confined within one direction, leading to a change in the shape of electronic density of states  $D(E)$ . Figure 1 shows  $D(E)$  as a function of energy  $E$  for 0D quantum dot, 1D nanowire, 2D superlattice and 3D bulk materials [9]. In contrast to the parabolic shape of  $D(E)$  for the bulk materials, the spike-like shape of  $D(E)$  for nanowires implies the increased electronic density states near the Fermi level, resulting in an increased thermal power factor  $S^2\sigma$ . Taking n-type materials

as an example, we can generally explain the enhancement in the thermal power factor  $S^2\sigma$  for nanowires by using the expression of the electron concentration

$$n = \int_0^{\infty} D(E)f(E_c - E_f)dE , \quad (1)$$

Where  $D(E)$  is the electronic density of states and  $f(E_c-E_f)$  is the Fermi-Dirac distribution function, and the expression of the Seebeck coefficient for n-type materials

$$S = -\frac{k_B}{e}(E_c - E_f + \frac{3}{2}k_B T) \sim (E_c-E_f), \quad (2)$$

Where  $E_c$  and  $E_f$  are the conduction band energy and the Fermi energy. It is clear from equation (2) that the Seebeck coefficient is large when the average electron energy is far away from the Fermi level. In semiconductors, a large Seebeck coefficient occurs when the Fermi level is inside the band-gap. A Fermi level deep inside the band-gap, however, leads to a low electrical conductivity. The optimized Fermi level usually is close to the band edge. Because the function  $\partial feq/\partial E$  is nonzero only in an energy range  $\sim k_B T$  near the Fermi level, the higher the DOS in this range, the larger power factor we can anticipate. In bulk materials, the parabolic shape of the DOS means that the electron density surrounding the Fermi level is small. In nanowire materials, the spikes in the DOS suggest that  $S^2\sigma$  can be increased. On the other hand, for the heavily doped semiconductors, the power factor is also larger for nanowires than for bulk materials. In this case, the electron concentration depends on the doping density. If the nanowire and the bulk materials are doped with the same doping density, then the two materials have the same electron density. From equation (1), however, a larger  $D(E)$  means a small  $f(E_c-E_f)$  and thus a larger  $(E_c-E_f)$ . As a result, the Seebeck coefficient of nanowires is higher

than that of bulk materials whereas the electrical conductivity is the same. Therefore, the power factor is enhanced in nanowire materials.

There have been extensive studies on quantum confinement effects on a number of different thermoelectric nanowire materials. In this paper we choose the efforts on bismuth (Bi) nanowires and bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) nanowires for a brief review.

## QUANTUM CONFINEMENT EFFECTS ON THERMOELECTRIC NANOWIRES

### 1. Bismuth nanowire systems

Bismuth is a very attractive material for low-dimensional thermoelectricity because of the very long mean free path of electrons and the high mobility of the carriers, which imply strong quantum confinement effects on carriers. Since the bulk Bi is semimetal, the contribution from the holes to the Seebeck coefficient, although pretty large, approximately cancels that from the electrons. Therefore the total  $S$  is quite small. However, when Bi materials shrink the size to be nanowires, they form subbands in the directions where quantum confinement occurs, and the resulting lowest quantized subband in the conduction band lies above the bulk conduction band extreme, and correspondingly the highest quantum subband in the valence band lies below the bulk valence band extreme. Furthermore, the shifting of the band edges depends on the sizes of nanowires [10]. Therefore, the band overlap between the valence and conduction bands, which is responsible for the semimetal behavior of bismuth, will vanish at some critical size where the semimetal-semiconductor transition occurs. In the semiconducting regime, single carrier transport can be achieved through doping, so bismuth nanowires may be made as good thermoelectric materials.

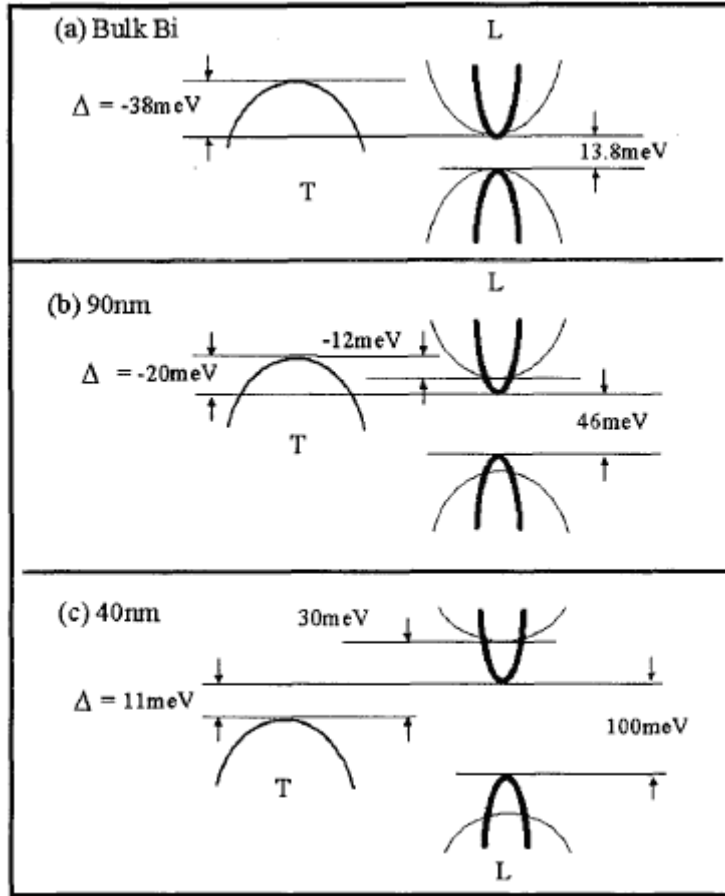


Figure 2. Schematic energy band diagram showing the energies of the subband edges for the heavy and light L-point electrons and for the T-point holes for: (a) bulk bi, (b) 90 nm-diameter Bi nanowires along the  $(10\bar{1}1)$  direction, and (c) 40 nm-diameter Bi nanowires along the  $(10\bar{1}1)$  direction.

In a theoretical study conducted by X. Sun [11], the conduction and valence subband edges at the  $L$ -point in the Brillouin zone are calculated using the Lax model for strongly coupled bands, while the energy subband edges for the  $T$ -point holes are found using a simple parabolic model. Figure 2 shows schematically the calculated ground-state energies of the lowest lying heavy electron and light electron  $L$ -point subbands and also the highest lying  $T$ -point hole subband for Bi nanowires oriented along the  $(10\bar{1}1)$

growth direction, in comparison to the bulk Bi band structure. Figure 2(b) shows that the 90 nm wire is a semimetal with a small band overlap of 20 meV, so that thermal energy (25 meV) is sufficient to cause significant occupation of the both electron subbands indicated in the figure. However, the 40 nm wire is a semiconductor and thermal excitation excites only the lowest lying electron subband. The size dependence of thermoelectric figure of merit of Bi nanowires is calculated based on the subband structure model for n-type Bi shown in figure 2, and the results at  $T = 77\text{ K}$  are shown in figure 3. It is clear that the n-type nanowires with diameters less than 10 nm are needed for thermoelectric applications, and even smaller diameters are needed for the p-type Bi nanowires [10].

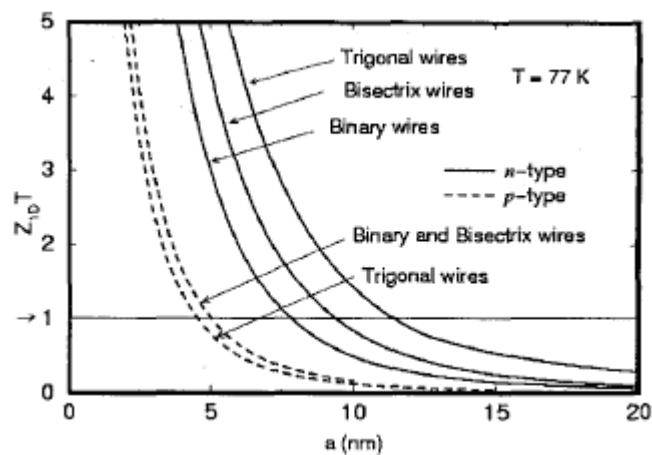


Figure 3. The thermoelectric figure of merit  $ZT$  for optimum carrier doping as a function of nanowire width  $a$ , at 77 K for both p-type and n-type Bi nanowires oriented along the three principal crystalline directions.

## 2. Bismuth telluride nanowire systems

Bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) nanowires have been an interest of researchers in the past decade because the best bulk thermoelectric materials are from bismuth and tellurium alloys. Assume that electrons (n-type  $\text{Bi}_2\text{Te}_3$  nanowires) are confined to move only along

$x$  direction like free electrons and are bounded in the  $y$  and  $z$  directions with infinite potential barriers, the electronic dispersion relation

$$\varepsilon(k_x) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 \pi^2}{2m_y a^2} + \frac{\hbar^2 \pi^2}{2m_z a^2} \quad (3)$$

can be used to calculate the transport coefficients of one band nanowires materials. Other assumptions to be considered in this simple model are that of a constant relaxation time  $\tau$ ,

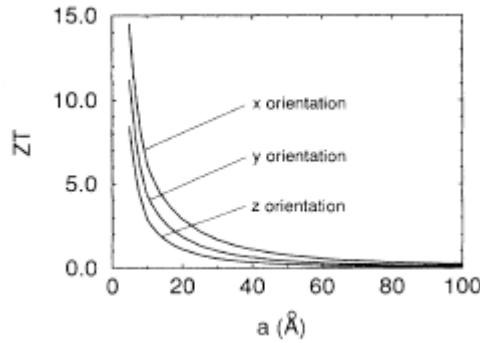


Figure 4. Plot of  $ZT$  vs wire width  $a$  for 1D  $\text{Bi}_2\text{Te}_3$  nanowires fabricated along the  $x$ ,  $y$  and  $z$  directions

and that of parabolic bands in the direction of conduction [12]. For  $\text{Bi}_2\text{Te}_3$  materials, there are six carrier pockets in the Brillouin zone and each of them has slightly different orientation. Figure 4 shows calculation results of  $ZT$  as function of the wire width  $a$  in  $x$ ,  $y$  and  $z$  directions. These results are obtained based on the simple assumption that all the six pockets have the same orientation. The mobility of electrons is assumed to be highest in  $x$  direction. From the calculation, it can be seen that  $ZT$  increases with decreasing  $a$  for nanowires in all three directions and it is higher in  $x$  direction than in other two directions. The start width for the significant increase in  $ZT$  is below a width of the order of the thermal de Broglie wavelength  $(\hbar^2 / 2m_i k_B T)^{1/2}$  for each orientation. A value of  $ZT \approx 14$  is calculated for a wire of width 5 angstrom oriented in the  $x$  direction.

CONCLUSION

Quantum confinement effects on Bi and Bi<sub>2</sub>Te<sub>3</sub> nanowire systems are reviewed in this paper. These effects result in an increased electronic density of states near the Fermi energy level, leading to an enhanced power factor in nanowire materials. Considering the reduction of thermal conductivity due to the rising phonon boundary scattering, thermoelectric nanowire materials, therefore, may have significantly improved thermoelectric figure of merit compared to their bulk counterparts.

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