RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 24 15 JUNE 1993-II

Thermoelectric figure of merit of a one-dimensional conductor

L. D. Hicks
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

M. S. Dresselhaus
Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 29 March 1993)

We investigate the effect on the thermoelectric figure of merit of preparing materials in the form of one-dimensional conductors or quantum wires. Our calculations show that this approach has the potential to achieve a significant increase in the figure of merit over both the bulk value and the calculated two-dimensional superlattice values.

For a material to be a good thermoelectric cooler, it must have a high thermoelectric figure of merit, ZT. The figure of merit is defined by[1]

$$ZT = \frac{S^2 \sigma T}{\kappa}\,, \tag{1}$$

where S is the thermoelectric power (Seebeck coefficient), σ is the electrical conductivity, and κ is the thermal conductivity. In order to achieve a high ZT, one requires a high thermoelectric power S, a high electrical conductivity σ, and a low thermal conductivity κ. In general, it is difficult to improve ZT for the following reasons. Increasing the thermoelectric power S for simple materials also leads to a simultaneous decrease in the electrical conductivity. Also, an increase in the electrical conductivity leads to a comparable increase in the electronic contribution to the thermal conductivity because of the Wiedemann-Franz law. So with known conventional solids, a limit is rapidly obtained where a modification to any one of these parameters adversely affects the other transport coefficients, so that the resulting ZT does not vary significantly. Currently, the materials with the highest ZT are Bi_2Te_3 alloys such as $Bi_{0.5}Sb_{1.5}Te_3$, with $ZT \simeq 1.0$ at 300 K.[1] Only small increases in ZT have been achieved in the last two decades, so it is now felt that the Bi_2Te_3 compounds may be nearing the limit of their potential performance.[2]

In an earlier paper,[3] we considered the effect on ZT of using materials in two-dimensional (2D) structures such as 2D quantum-well superlattices. We showed that this approach could yield a significant increase in ZT. Recently, new fabrication technology has made it possible to confine an electron gas to *one* dimension,[4] thus making it possible to produce a one-dimensional conductor. Within the last few months, one-dimensional conductors were obtained by a different method: the encapsulation of metal filaments in carbon nanotubes.[4,5] Some of these tubes are 1.5 nm in diameter,[5] so it is now possible to fabricate very narrow quantum wires. In this paper, we investigate theoretically the effect on ZT of using materials in the form of 1D conductors or quantum wires. These structures will significantly alter ZT since the electrons are now confined to move in a single dimension. In addition there will be increased phonon scattering from the surfaces of the wires. This will lead to a reduction in the lattice thermal conductivity and hence an increase in ZT.

Expressions for S, σ, and κ have been derived for transport in a 1D quantum wire. The calculations are for a general, anisotropic, one-band[6] material (assumed for convenience to be the conduction band). The only other assumptions are that of a constant relaxation time τ, and that of parabolic bands in the direction of conduction. Note that the calculation is *not* restricted to semiconductors. The material can be a metal, semiconductor, or semimetal, as long as it is effectively a one-band material. A similar method was used in Ref. 3 to derive expressions for ZT of a 3D bulk material and a 2D quantum well. The 3D results agreed well with the experimental values for Bi_2Te_3, so the assumptions are likely to be valid.

Let the conductor be square in cross section, with a side of length a. Take the current to flow in the x direction. General expressions in Ref. 7 were used to derive the transport coefficients for a 1D conductor. The electronic dispersion relation used is

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

indicating free-electron-like motion in the x direction and a bound state (for infinite potential barriers) in the y and z directions. Note that only the lowest subband has been considered in Eq. (2). This is consistent with the original assumption of a one-band model. The results for the transport coefficients are shown below:

$$\sigma = \frac{1}{\pi a^2}\left(\frac{2k_B T}{\hbar^2}\right)^{1/2} m_x^{1/2} F_{-1/2}\, e\mu_x\,, \tag{3}$$

$$S = -\frac{k_B}{e}\left(\frac{3F_{1/2}}{F_{-1/2}} - \eta\right), \tag{4}$$

$$\kappa_e = \frac{2\tau}{\pi a^2}\left(\frac{2k_BT}{\hbar^2}\right)^{1/2} m_x^{-1/2}k_B^2T\left(\frac{5}{2}F_{3/2} - \frac{9F_{1/2}^2}{2F_{-1/2}}\right), \tag{5}$$

where $\eta = \zeta/k_BT$ is the reduced chemical potential (ζ is the chemical potential *relative to the lowest bound state*), τ is the relaxation time, m_x, m_y, m_z are the effective mass components, μ_x is the mobility in the x direction, and κ_e is the electronic thermal conductivity. The Fermi-Dirac functions F_i are given by

$$F_i = F_i(\eta) = \int_0^\infty \frac{x^i dx}{e^{(x-\eta)}+1}. \tag{6}$$

So, using

$$ZT = \frac{S^2\sigma T}{\kappa_e + \kappa_L}, \tag{7}$$

where κ_L is the lattice thermal conductivity gives

$$ZT = \frac{\frac{1}{2}\left(\frac{3F_{1/2}}{F_{-1/2}} - \eta\right)^2 F_{-1/2}}{\frac{1}{B} + \frac{5}{2}F_{3/2} - \frac{9F_{1/2}^2}{2F_{-1/2}}}, \tag{8}$$

where

$$B = \frac{2}{\pi a^2}\left(\frac{2k_BT}{\hbar^2}\right)^{1/2}\frac{k_B^2Tm_x^{1/2}\mu_x}{e\kappa_L}. \tag{9}$$

For a given value of B, the reduced chemical potential $\eta = \zeta/k_BT$ may be varied to change the value of ZT. The maximum value of ZT occurs when η is equal to its optimal value, η^*. B is determined largely by the intrinsic properties of the material, but η may be varied by doping. To maximize ZT for a material, one first calculates B for the intrinsic material, then determines the value of η^*, which maximizes ZT for this value of B. The next step is to adjust η so that $\eta = \eta^*$: this may be achieved by doping. It may be necessary to keep the dopant ions spatially removed from the conduction path to avoid impurity scattering. This form of doping (modulation doping) has been used in 2D quantum-well heterostructures. $ZT(\eta^*)$ rises monotonically with B, so it is necessary to maximize B in order to achieve the maximum ZT. Since $\mu_x \sim m_x^{-1}$, $B \sim \mu_x^{1/2}$, so the highest mobility direction will give the highest B. Also, $B \sim a^{-2}$, so a narrower wire will give a higher B and hence a higher ZT.

One of the best materials for thermoelectric refrigeration is Bi_2Te_3, with a bulk ZT of 0.7 at 300 K.[1] The expressions derived previously are now used to calculate ZT for Bi_2Te_3 in a 1D quantum-wire structure.

Bi_2Te_3 has a trigonal structure, which can be expressed in terms of a hexagonal unit cell of lattice parameters $a_0 = 4.3$ Å and $c_0 = 30.5$ Å.[1] The compound has an anisotropic effective mass tensor, with components $m_x = 0.02m_0$, $m_y = 0.08m_0$, and $m_z = 0.32m_0$.[8] The lattice thermal conductivity is $\kappa_L = 1.5\ \mathrm{W\,m^{-1}\,K^{-1}}$ and the mobility along the a_0 or x axis is $\mu_x = 1200\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$.[1]

The equation for ZT derived so far assumed a single carrier pocket in the Brillouin zone of the bulk material. For multiple pockets, the value of B in Eq. (9) needs to be multiplied by a number of the order of the number of pockets. Bi_2Te_3 has six carrier pockets, each with a slightly different orientation in the Brillouin zone.[8] In our earlier paper,[3] in order to make simple numerical estimates of ZT for both bulk and superlattice Bi_2Te_3, we assumed that all six pockets have the same orientation. This assumption in fact gave a value for bulk ZT in good agreement with the experimental value. In order to make numerical estimates of ZT for one-dimensional Bi_2Te_3, we made the same assumption. This consistent approach enabled us to make direct comparisons between the calculated values of ZT for 3D, 2D, and 1D Bi_2Te_3. The exact values of the parameters of Bi_2Te_3 are not of crucial importance since the material is used mainly as an illustration of the effect on ZT of going to lower dimensions. Since six carrier pockets are assumed for 1D Bi_2Te_3, the expression for B becomes

$$B = 6\frac{2}{\pi a^2}\left(\frac{2k_BT}{\hbar^2}\right)^{1/2}\frac{k_B^2Tm_x^{1/2}\mu_x}{e\kappa_L}. \tag{10}$$

If the wire is fabricated for conduction along the y or z axes, then the variable $m_x^{1/2}\mu_x$ is replaced by $m_y^{1/2}\mu_y$ or $m_z^{1/2}\mu_z$, respectively.

In a 1D quantum wire, as the electrons are confined to 1D motion parallel to the wire, there is no scattering off the surface, so the mobility in the direction parallel to the wire is unchanged.[9] However, phonons in Bi_2Te_3 still move in three dimensions, so that they may scatter off the surface. In thin wires this will reduce the lattice thermal conductivity. Now

$$\kappa_L = \tfrac{1}{3}C_v v l, \tag{11}$$

where l is the mean free path, C_v is the lattice heat capacity, and v is the velocity of sound in the material. For Bi_2Te_3, $C_v = 1.2\times10^6\ \mathrm{J\,K^{-1}\,m^{-3}}$ and $v = 3\times10^3\ \mathrm{m\,s^{-1}}$,[10] giving a value of $l = 10$ Å. If the wire thickness a is greater than 10 Å, then surface scattering does not seriously affect the mean free path l, and κ_L should then be the same as its bulk value. This is a conservative assumption used to make numerical estimates for ZT, as surface scattering will still occur for $a > 10$ Å; this scattering will cause a slight decrease in κ_L and an increase in ZT. If a is less than 10 Å, then l and κ_L are limited by surface scattering and a good estimate for κ_L is obtained by setting $l = a$ and using Eq. (11). From the expression for B in Eq. (10), decreasing the wire thickness a increases B, and therefore increases ZT. Also, if $a < 10$ Å, then κ_L is reduced from its bulk value, resulting in an additional increase in ZT. So to achieve the best ZT, it is necessary to make the wire as narrow as possible.

When calculating η^* for a material, one must check that it does not lie above the energy of the next-to-lowest subband of the quantum wire. If η^* does indeed lie above

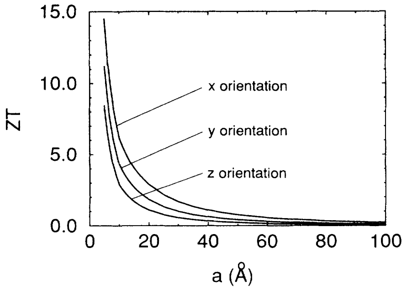

FIG. 1. Plot of $ZT(\eta^*)$ vs wire width a for 1D wires fabricated along the x, y, and z directions.

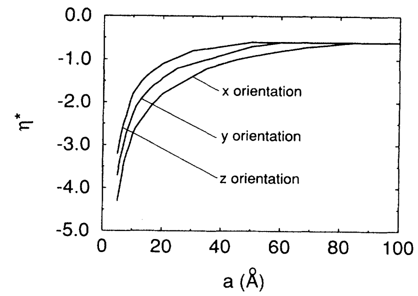

FIG. 2. Plot of η^* vs wire width a for 1D wires fabricated along the x, y, and z directions.

the energy of the next subband, then more than one subband will contribute significantly to ZT: this is inconsistent with the assumption of a one-band system and one would need to extend the model in order to get meaningful results.

$ZT(\eta^*)$ was calculated as a function of width a for quantum wires of Bi_2Te_3 fabricated along the x, y, and z directions. The mobilities μ_y and μ_z were estimated using the fact that $m_x\mu_x = m_y\mu_y = m_z\mu_z$. The results of the calculations are shown in Fig. 1, with the corresponding values of η^* in Fig. 2. The calculations were done for values of a starting from 5 Å, since it is unlikely that much narrower wires can be made for Bi_2Te_3 since the a_0 dimension of the unit cell is 4.3 Å.[1] For values of $a < 10$ Å, κ_L was estimated using Eq. (11) with $l = a$.

Before any conclusions can be drawn, it is necessary to check the validity of the results by making sure that η^* does indeed lie below the energy of the second subband. From Fig. 2, η^* is always negative, so it lies even lower than the *lowest* subband, so the results calculated using a one-band model are valid.

From Fig. 1, for a given value of a, ZT for the wire in the x direction is always higher than for the other two directions. This is expected since the highest mobility direction is along the x axis. For all three orientations, ZT increases with decreasing a. ZT starts to increase significantly when a drops below a width of the order of the thermal de Broglie wavelength $(\hbar^2/2m_ik_BT)^{1/2}$ for each orientation. A value of $ZT \simeq 14$ was calculated for a wire of width 5 Å oriented in the x direction. In a previous paper,[3] we calculated the best ZT for bulk Bi_2Te_3 to be $Z_{3\mathrm{D}}T = 0.5$.[11] For a 2D quantum well of width 10 Å, the best calculated figure of merit was $Z_{2\mathrm{D}}T = 2.5$, and for a 5-Å quantum well, $Z_{2\mathrm{D}}T = 5$. For comparison, the best calculated ZT for a 10-Å-wide quantum wire is $Z_{1\mathrm{D}}T = 6$ and for a 5-Å wire, $Z_{1\mathrm{D}}T = 14$. So the maximum ZT for a 1D wire is greater than ZT for both the bulk material and for a 2D quantum well. These results indicate that a significant increase in ZT can be achieved by going to lower dimensions, with the highest ZT occurring in one dimension. This increase is due mainly to the change in the density of states, but an additional factor is the reduced lattice thermal conductivity due to increased phonon surface scattering.

It may not be easy, however, to fabricate one-dimensional wires of Bi_2Te_3 of the required thickness. The best hope seems to lie with the technique of encapsulating materials in carbon nanotubes, since some of these tubes have the necessary narrow diameters of about 1.5 nm.[5]

In conclusion, the thermoelectric figure of merit of a one-dimensional conductor or quantum wire depends strongly on the width of the wire. For widths narrower than the order of the thermal de Broglie wavelength of the carriers, the figure of merit increases significantly with decreasing a. If Bi_2Te_3, the best present thermoelectric material, is made in the form of a 1D wire, then a ZT of up to 14 is predicted for a wire of square cross section and width 5 Å. The results of this calculation show that quantum-wire structures have the potential to significantly improve the thermoelectric figure of merit above the best present values.

The authors would like to thank G. Dresselhaus for useful discussions, and T. Harman and J. Farmer for their suggestions. We gratefully acknowledge support for this work by the U.S. Navy under Contract No. N00167-92-K0052.

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[7] One-band materials (such as doped semiconductors) give the best ZT. The reasons for this are explained in Refs. 1 and 3.

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[10] This is actually a conservative estimate since it is likely that the 1D mobility will be higher than the 3D mobility due to

the reduction in the range of phonon wave vectors that can participate in electron-phonon scattering. A higher μ_x will give a higher B and therefore a higher ZT than we have calculated.

[11] H. H. Landolt and R. Börnstein, *Numerical Data and Functional Relationships in Science and Technology* (Springer-Verlag, Berlin, 1983), Vol. 17f, pp. 272–278.

[12] This compares favorably with the experimental value of $ZT = 0.7$ (Ref. 1).