Low Dimensional Thermoelectric Materials

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The promise of low dimensional thermoelectric materials for enhanced performance is reviewed, with particular attention given to quantum wells and quantum wires. The high potential of bismuth as a low dimensional thermoelectric material is discussed.

Professor Abram Ioffe and his collaborators at the Ioffe Institute in St. Petersburg, Russia did pioneering work [1] in introducing semiconductors as promising thermoelectric materials and in showing how semiconductors could be used in practical devices for cooling and for electrical power generation [1]. This early work led to a very active period in thermoelectrics research in the 1950s and early 1960s, when many new thermoelectric materials were discovered and investigated. At this early time, the high potential of Bi_2Te_3 as a thermoelectric material was discovered by H. J. Goldsmid and coworkers in the U.K. [2], and this material system remains the basis for the thermoelectric industry up to the present time [3]. Ioffe's proposal to employ semiconductor alloys rather than simple binary compounds in order to lower the thermal conductivity of semiconductors [4] proved very useful for thermoelectric applications, thereby leading to the industrial use of alloys in the Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 family.

For a 30 year period since the early 1960s, research activity in the field of thermoelectricity has been greatly reduced, and only modest progress was made in improving the performance of thermoelectric materials [3]. Recently, the study of thermoelectric materials has once again become an active research field, in part due to the recent demonstration of enhancement in the thermoelectric figure of merit of a two-dimensional PbTe quantum well system, relative to its three-dimensional (3D) bulk counterpart [5]. Calculations suggest that the thermoelectric performance of any 3D material should show an enhanced thermoelectric figure of merit, when prepared as a 2D multi-quantum well superlattice, utilizing the enhanced density of states at the onset of each electronic subband, and the increased scattering of vibrational waves at the boundary between the quantum well and the adjacent barrier of the superlattice. In addition, low dimensionality allows certain materials such as bismuth, which are poor thermoelectrics in 3D, to become good thermoelectrics, in principle, in 2D quantum well or 1D quantum wire structures.

It is customary to express the usefulness of a thermoelectric material for use in refrigeration or power generation applications in terms of the dimensionless quantity ZT where T is the temperature (in degrees Kelvin) and Z is the thermoelectric figure of merit

$$Z = \frac{S^2\sigma}{\kappa}. \qquad (1)$$

Here S is the thermoelectric power or Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. Large values of ZT require high S, high σ, and low κ. Since an increase in S normally implies a decrease in σ because of carrier density considerations, and since an increase in σ implies an increase in the electronic contribution to κ as given by the Wiedemann–Franz law, it is very difficult to increase Z in typical thermoelectric materials. The best commercial 3D thermoelectric material is in the $Bi_{2(1-x)}Sb_{2x}Te_{3(1-y)}Se_{3y}$ family with room temperature $ZT \approx 1$ for $Bi_{0.5}Sb_{1.5}Te_3$ [3].

Reduced dimensionality offers one strategy for increasing ZT relative to bulk values [6,7]. The use of low dimensional systems for thermoelectric applications is of interest because low dimensionality provides: (1) a method for enhancing the density of states near E_F, leading to an enhancement of the Seebeck coefficient, (2) opportunities to take advantage of the anisotropic Fermi surfaces in multi-valley cubic semiconductors, (3) opportunities to increase the boundary scattering of phonons at the barrier-well interfaces, without as large an increase in electron scattering at the interface, (4) opportunities for increased carrier mobilities at a given carrier concentration when quantum confinement conditions are satisfied, so that modulation doping and δ-doping can be utilized.

1. Theoretical Modeling

In early models for thermoelectricity in 2D quantum well structures [6–9] it was assumed that the electrons in the valence and conduction bands are in simple parabolic energy

bands and that the electrons occupy only the lowest subband of the quantum well. The electronic dispersion relations for a 2D system are then given by

$$\mathcal{E}_{2D}(k_x, k_y) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 \pi^2}{2m_z d_W^2}, \qquad (2)$$

where d_W is the width of the quantum well, and m_x, m_y, and m_z are the effective mass tensor components of the constant energy surfaces. It is further assumed that the current flows in the x direction and that quantum confinement is in the z direction. The corresponding relation used for a square 1D quantum wire is

$$\mathcal{E}_{1D}(k_x) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 \pi^2}{2m_y d_W^2} + \frac{\hbar^2 \pi^2}{2m_z d_W^2}, \qquad (3)$$

where the current flow is also along the x direction, and quantum confinement occurs in the y and z directions. Solutions of Boltzmann's equation were then obtained for S, σ, and κ_e (the electronic contribution to the thermal conductivity) for both the 2D and 1D systems [6,9–11].

2. Experimental Proof-of-Prinsiple

An early phase of the experimental work was devoted to showing proof-of-principle [5], in order to confirm the validity of the basic theoretical model for low dimensional thermoelectric materials [6,9]. PbTe was chosen as the quantum well material for demonstrating proof-of-principle of an enhanced ZT in a 2D system because of its desirable thermoelectric and materials science properties [12,13]. Regarding its thermoelectric properties, PbTe has a reasonably high ZT at 300 K in bulk form ($ZT \simeq 0.4$), reflecting its high carrier mobility, multiple anisotropic carrier pockets, and low thermal conductivity that can be achieved under isoelectronic alloying. Measurements of $S^2\sigma$ by Hicks *et al.* [5] corroborated that quantum confinement could be achieved in a PbTe/$Pb_{1-x}Eu_xTe$ superlattice, for $x = 0.073$, by using large barrier widths $d_b \gg d_W$. Good agreement between experiment and theory was demonstrated in plots of $S^2\sigma$ as a function of carrier concentration and quantum well width, thereby corroborating the model, using no adjustable parameters (only literature values measured by other techniques) [5]. High carrier mobilities were found for these superlattice samples [5].

3. Recent 2D Superlattice Studies

Having demonstrated experimental evidence in support of the basic theoretical model, the focus of research on low dimensional thermoelectricity has shifted to two new directions. One research direction focused on observations of the enhancement of ZT in other 2D superlattice systems, so that the basic phenomenon could then be studied in more detail, and the barrier widths could be reduced, noting that the barrier regions contribute only to κ in Eq. (1) and not to the power factor $S^2\sigma$. Some of the systems that were studied include p-type PbTe, where power factors higher than for n-type PbTe were reported, while at the same time using d_b/d_W ratios reduced by a factor of more than two, relative to n-type PbTe [14]. Another superlattice system that was studied was the Si/SiGe system, where an increase in the room temperature power factor of the superlattice relative to the bulk silicon value was predicted, and where even better performance could be expected at elevated ($\gg$ 300 K) temperatures [15].

As a second approach, emphasis was given to achieving higher $Z_{3D}T$ for the whole superlattice sample (both for the quantum well and barrier regions) and to studying superlattices which do not show quantum confinement effects [16]. By using the same basic model, as was developed for the PbTe/$Pb_{1-x}Eu_xTe$ superlattice, to study the GaAs/AlAs superlattice, it was shown that when the d_W and d_b values are sufficiently small, the electronic density of states is basically two-dimensional in both the quantum well and barrier regions [17], and an increase in power factor relative to bulk values could be achieved. One great advantage of allowing conduction in both the barrier and the quantum well region is that much shorter barrier widths can be used and a significant contribution to $S^2\sigma$ from the barrier region can be obtained. The gains in $S^2\sigma$ from the quantum well region relative to bulk values more than compensate for the somewhat lower contribution to $S^2\sigma$ from the barrier region, so that $S^2\sigma$ for the whole superlattice (denoted by $Z_{3D}T$) exceeds that of the bulk. In addition, a large reduction in thermal conductivity is expected, due to the strong interface phonon scattering, so that significant increases in $Z_{3D}T$ are expected from this approach.

Calculations suggest that another effect that may come into play relates to carrier pocket engineering, whereby by proper selection of d_W, d_b and their ratio (d_b/d_W), it is possible to raise the energy of the lowest Γ point subband so that it lies higher than the L and X point subbands, thereby leading to an enhancement of $Z_{3D}T$ because of the high density of states for the L and X point subbands [17]. Simple calculations suggest that such carrier pocket engineering can be carried out in the case of GaAs/AlAs superlattices with d_W and d_b in the 20–30 Å range [17].

Experimentally, enhancement in the power factor and $Z_{3D}T$ have been reported for several superlattice systems not exhibiting quantum carrier confinement effects, including the Bi_2Te_3/Bi_2Se_3 [16], PbTe/$PbSe_{1-x}Te_x$/Te ($x = 0.02$) [18], and Si/Ge systems [19]. In fact, the highest ZT value ever reported for any thermoelectric material is $Z_{3D}T = 1.9$ for the PbTe/$PbSe_{1-x}Te_x$/Te system ($x = 0.02$) at 570 K [18]. It is expected that we will see considerably more activity in the near future, both experimentally and theoretically, on the study of such composite superlattice systems, which may exhibit some type of lower dimensional electronic properties, but do not exhibit significant carrier quantum confinement.

4. Bismuth as a Low Dimentional Thermoelectric

Bismuth is a very attractive material for low dimensional thermoelectricity because of the large anisotropy of the three ellipsoidal constant energy surfaces for electrons at the L point in the rhombohedral Brillouin zone ($m_x^* = 0.00651m_0$, $m_y^* = 1.362m_0$, $m_z^* = 0.00993m_0$), the very long mean free path of the L-point electrons, and the high mobility of the carriers ($\mu = 3.5 \times 10^4$ cm^2/Vs in the binary direction) [20]. Furthermore, the heavy mass of the Bi ions results in efficient phonon scattering and low phonon mean free paths. Since bulk bismuth is a semimetal, the contribution from the holes to the Seebeck coefficient approximately cancels that for the electrons, so that S is quite small, and high magnetic fields are needed to make bulk Bi interesting for thermoelectric applications [21].

The situation for 2D Bi in a quantum well is, however, quite different. As the quantum well width decreases, the lowest bound state in the conduction band rises above the highest bound state in the valence band, thereby leading to a semimetal-semiconductor transition at some critical value of d_W [11]. If the 2D bismuth system is then doped to the optimum doping level, a large enhancement in $Z_{2D}T$ within the quantum well is predicted with decreasing d_W, as shown in the plot of $Z_{2D}T$ vs d_W in Fig. 1 for a Bi superlattice normal to the trigonal direction, for which all the electron carrier pockets are equivalent. Considerable progress has been made recently by use of CdTe as a barrier material for synthesizing Bi quantum wells [22]. While study of 2D Bi superlattices continues, recent effort has also been expended to study 1D bismuth nanowires [23,24]. Calculations for transport in the trigonal direction indicate that 1D bismuth nanowires with very small wire diameter could be even better than 2D bismuth for thermoelectric applications (see Fig. 1).

Although no enhancement in ZT has yet been demonstrated experimentally with Bi nanowires, progress has been made toward making proof-of-principle studies of this system. Small diameter Bi wires have been successfully fabricated by pressure-injecting liquid Bi into the cylindrical nano-channels of a porous anodic alumina template [23]. Such anodic alumina templates with pore diameters ranging from 13–110 nm have been filled with liquid Bi to reach a density as high as 7×10^{10} parallel wires/cm^2, with template thicknesses and wire lengths up to 100 μm. As shown by high resolution electron microscopy and selected area electron diffraction experiments, the individual Bi nanowires are essentially single crystals, with nearly the same crystal structure and lattice parameters as bulk Bi. The individual wires are of uniform diameter along their entire length, and the nanowires in a given template have a similar crystalline orientation along their common wire axes [23]. The large bandgap of the anodic alumina host material ensures good carrier quantum confinement. Optical transmission [23] and magnetoresistance studies [24–26] provide evidence for a semimetal to semiconducting transition as the wire diameter decreases and reaches the critical diameter d_c, below which a semiconducting gap is found. Our theoretical calculations, based on values of the effective masses for bulk bismuth, indicate on the basis of a simple parabolic band model for the electron states, that for the binary, trigonal and bisectrix directions, $d_c \approx 30$ nm, 45 nm and 81 nm, respectively [24].

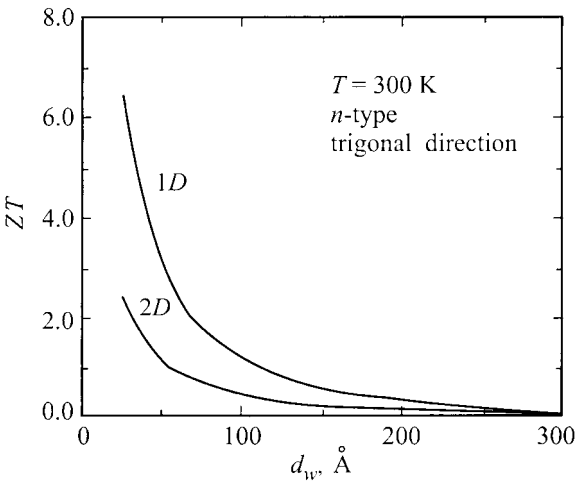

Figure 1. Dependence of $Z_{2D}T$ and $Z_{1D}T$ on quantum well and quantum wire widths d_W for the layers of the Bi quantum wells normal to the trigonal direction and the Bi wire axis along the trigonal direction.

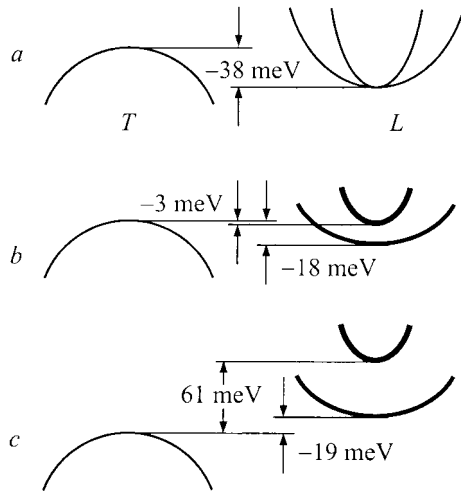

Figure 2. Schematic energy band diagram showing the energies of the subband edges for the heavy and light electrons and for the holes for: (a) bulk Bi, (b) 100 nm diameter Bi nanowires along the bisectrix direction, and (c) 50 nm diameter Bi nanowires along the bisectrix direction.

Fig. 2 shows a schematic diagram of the electronic energy band structure for bismuth nanowires in comparison to bulk bismuth, which is a semimetal with electrons in 3 carrier pockets at the L points in the rhombohedral Brillouin zone and holes in a single carrier pocket at the T point, and the band overlap of bulk Bi is 38 meV [20]. For Bi nanowires oriented along the bisectrix direction, there are two electron pockets in which the electrons have a heavy cyclotron effective mass (m_c^h) and one electron pocket with a light cyclotron effective mass (m_c^l), where the cyclotron mass is an average for the in-plane motion. Fig. 2, *b*, and *c* show

schematically the calculated ground state energies of the heavy electron and light electron subbands and also the hole subband for a Bi wire oriented along the bisectrix direction with a diameter of 100 nm and 50 nm, respectively, in comparison to the bulk Bi band structure shown in fig. 2, *a* [24]. Here we see that the lowest heavy electron subband lies lower than the corresponding light electron subband. The figure further shows that the 100 nm wire is a semimetal with a small band overlap of 3 meV, and thermal energy (25 meV) is sufficient to cause significant occupation of the light electron subband. However, the 50 nm diameter wire along the bisectrix direction is a semiconductor and thermal excitation excites only heavy electrons. Thus, we can expect rather different transport properties for a 100 nm and a 50 nm diameter wire.

Experimental transport studies are in progress to verify the predictions of the model for semiconducting bismuth for small wire diameters. In the semiconducting regime, work is in progress to estimate the thermoelectric properties of the bismuth nanowires theoretically and to measure them experimentally, focusing on the conditions needed for realizing an enhancement in ZT.

5. Conclusions

Some of the recent achievements that have been made in the use of low dimensional materials for thermoelectric applications include a $ZT \sim 1.2$ within *n*-type PbTe quantum wells at room temperature [5]. Higher values are expected for this system at higher temperatures. The highest value of ZT for any thermoelectric material under any conditions ($ZT > 1.9$) was achieved for a $PbTe/PbSe_{0.98}Te_{0.02}/Te$ superlattice at 570 K [18] where the system showed no quantum confinement effects. Since research in this field is still at an early stage of development, significantly more progress in enhancing ZT further is expected for the future. It is thus appropriate to review recent progress on thermoelectric materials in celebration of the 80th birthday of the Ioffe Institute, which has made so many important historical contributions to the field of thermoelectricity.

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