Material Optimization for Heterostructure Integrated Thermionic Coolers

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Abstract

The material figure-of-merit for conventional thermoelectrics is $\mu\, m_{eff}^{1.5}/\beta$ where μ is the electron or hole mobility, m_{eff} its effective mass, and β the material thermal conductivity. From the electronic point of view, in order to optimize the cooler performance, there is a trade off between electron effective mass and its mobility. While high mobility is inherently important to facilitate electron transport in the material and reduce the Joule heating, a large effective mass is only required due to the *symmetry* of electronic density-of-states with respect to the Fermi energy in an energy range on the order of thermal energy (k_B*T) near the Fermi level. It is possible to increase this asymmetry by using doping densities so that the Fermi level is close to the bandedge. In this case there is a small number of electrons participating in the conduction and the net transport of heat is small. We clarify how this trade off is alleviated in high barrier thermionic coolers. Prospects for different material systems to realize bulk and superlattice thermionic coolers are also discussed.

Introduction

The expressions of the electrical conductivity and the Seebeck coefficient can be written as:

$$\sigma = \frac{e^2}{4\pi^3}\iiint \tau(k) v_x^{\,2}(k)\left(-\frac{\partial f_{eq}}{\partial E}\right) d^3k \equiv \int \sigma(E)\left(-\frac{\partial f_{eq}}{\partial E}\right) dE$$

$$S = \frac{1}{eT}\frac{\iiint \tau(k) v_x^{\,2}(k)(E(k)-E_F)\left(-\frac{\partial f_{eq}}{\partial E}\right) d^3k}{\iiint \tau(k) v_x^{\,2}(k)\left(-\frac{\partial f_{eq}}{\partial E}\right) d^3k} \equiv \frac{k_B}{e}\frac{\int \sigma(E)\frac{(E-E_F)}{k_B T}\left(-\frac{\partial f_{eq}}{\partial E}\right) dE}{\int \sigma(E)\left(-\frac{\partial f_{eq}}{\partial E}\right) dE} \propto < E - E_f >$$

where we introduce the "differential" conductivity [1-3]:

$$\sigma(E) \equiv e^2 \tau(E) \iint v_x^{\,2}(E, k_y, k_z) dk_y dk_z \cong e^2 \tau(E) \bar{v}_x^{\,2}(E) \bar{n}(E)$$

Here $\tau(E)$ is the energy dependent relaxation time, $\bar{v}_x(E)$ the average velocity of the carriers with energy between E and $E+dE$ in the direction of current flow, and $\bar{n}_x(E)$ the number of electrons in this energy interval. Electrical conductivity is the sum of the contribution of electrons with various energies E (given by $\sigma(E)$ the differential conductivity) within the Fermi window factor $\partial f_{eq}/\partial E$. The Fermi window is a direct consequence of the Pauli exclusion principle; at finite temperatures only electrons near the Fermi surface contribute to the conduction process. In this picture the Seebeck coefficient is the average energy transported by the charge carriers corresponding to a diffusion thermopower. This transported energy can be increased with the coupling of other transport energies such as phonons to the electronic transit. In conventional thermoelectric coolers, the overall device performance is given by the dimensionless figure of merit $ZT = S^2\sigma T / \beta$, that describes the tradeoffs between the Peltier cooling given by the Seebeck coefficient (S), the Joule heating given by the electrical conductivity (σ), and the heat conduction from the hot to cold junction given by the thermal conductivity (β). It is this Z-factor that must be maximized to reach optimum performance and efficiency. At room temperature, conventional semiconductors have a thermal conductivity that is dominated by the lattice contribution, therefore maximizing Z necessitates maximizing the power factor $S^2\sigma \approx |\langle E - E_f \rangle|^2 \sigma$. Hence the differential conductivity, $\sigma(E)$, should be *large* within the Fermi window and be as *asymmetric* as possible with respect to the Fermi energy [11,27].

Material optimization for traditional thermoelectrics

By optimizing the doping in the expressions for electrical conductivity and Seebeck coefficient, one can find that the following ratio of material parameters needs to be optimized [1-5]:

$$\left(\frac{\mu . m^{*1.5}}{\beta} \cdot T_C^{\,2.5} \right)$$

When electrons move from a material in which their average transport energy is below the Fermi level, to another one in which their transport energy is increased, the electron gas will absorb thermal energy from the lattice and the junction between the two materials will be cooled (see Fig. 1). Reversing the direction of current will instead generate heat and will create a hot junction signifying a reversible heat engine. The dependence on electron mobility in the material figure-of-merit expression reflects the importance of unimpeded electron transport in the material to reduce the Joule heating. The requirement for large effective mass is due to the symmetry of the electronic density of states with respect to the Fermi energy over an energy range that is on the order of thermal energy (k_B*T) (see Fig. 1). The asymmetry may be increased by doping the material such that the Fermi level is close to the band edge, however this results in a small number of electrons taking part in conduction and a small amount of heat transported. Another more promising way to increase the asymmetry is to use thermionic emission current in heterostructures.

Small barrier heterostructure integrated thermionic (HIT) coolers

Using conduction (n-type) or valence (p-type) band offsets at heterostructures, the transport energy of electrons can be made to be almost entirely on one side of the Fermi level resulting in strong asymmetry [6-15]. In a simplified model [9-10] that neglects the finite electron energy relaxation length, the maximum cooling temperature by heterostructure thermionic emission can be expressed as:

$$\Delta T_{\max} = T_C \left(\sqrt{1 + \frac{\lambda k_B}{2e\beta} \left(\frac{e\Phi_C(I, T_C)}{k_B T_C} + 2 \right)^2 I} - 1 \right)$$

where T_c is the cold side temperature, Φ_c cathode barrier height, I current, λ electron mean free path in the barrier, and β the thermal conductivity of the barrier layer. By maximizing this equation with respect to current, one can find out that the material dependence of ΔT_{max} is only through the ratio $\lambda m^*/\beta$ or $\mu m^{*1.5}/\beta$, where μ is the carrier mobility in the barrier region.

$$\Delta T_{\max}\Big|_{I_{small}} \propto \left(\frac{\mu . m^{*0.5} \left[\ln(m^*/m_0) \right]^2}{\beta} \cdot T_C^{\,1.5} \left[\ln(T/T_0) \right]^2 \right)$$

$$\Delta T_{\max}\Big|_{I_{\max}} = T_C \left(\sqrt{1 + \frac{8\sqrt{3}\pi k_B^{\,3.5}}{\sqrt{2} e h^3} \cdot \frac{\mu . m^{*1.5}}{\beta} \cdot T_C^{\,2.5}} - 1 \right)$$

Interestingly, in this approximation, thermionic emission cooling and thermoelectric cooling have the same material figure of merit, and so through selective emission of hot carriers in heterostructures we can improve the cooling capacity of conventional thermoelectric materials. Fig. 2 shows this material figure of merit for several different semiconductor systems. SiGe is already an important thermoelectric material for high temperatures (> 900°C), and is an attractive material for thermionic cooling at room temperature. BiTe, the dominant thermoelectric material at room termperature, is also a good candidate for thermionic cooling, but the crystal growth and processing technology is not as mature as SiGe. Other materials such as InGaAs and HgCdTe are well suited for integration with optoelectronic devices and infared detectors respectively. While these latter two material systems have a material figure-of-merit that is roughly an order of magnitude smaller, thermionic cooling relaxes the requirement for high thermopower since the band edge discontinuities perform the work of creating large asymetries in the transport energy. The barrier material should simply have an adequate electrical conductivity and a low thermal conductivity, making ternary and quartenary semiconductors good candidates. In the above analysis, multiple valleys or carrier pockets are not considered. These can significantly change the asymmetry of electronic density-of-states, but at the same time the electron energy relaxation length is altered [11]. Thus a more detailed study is needed in order to evaluate the effects of multiple valleys on thermionic emission cooling in submicron devices. The restraint on thermal conductivity could also be aleviated if the hot electrons could lose their energy by light emission as previously proposed [9-10]. In this case a high thermal conductivty material would be benificial.

Large barrier HIT coolers

In large barrier HIT coolers the band offset is made as large as possible and the doping is such that the Fermi level is a few k_B*T below the wide bandgap material. Consequently the electronic density of states is greatly increased allowing more charge carriers to participate in

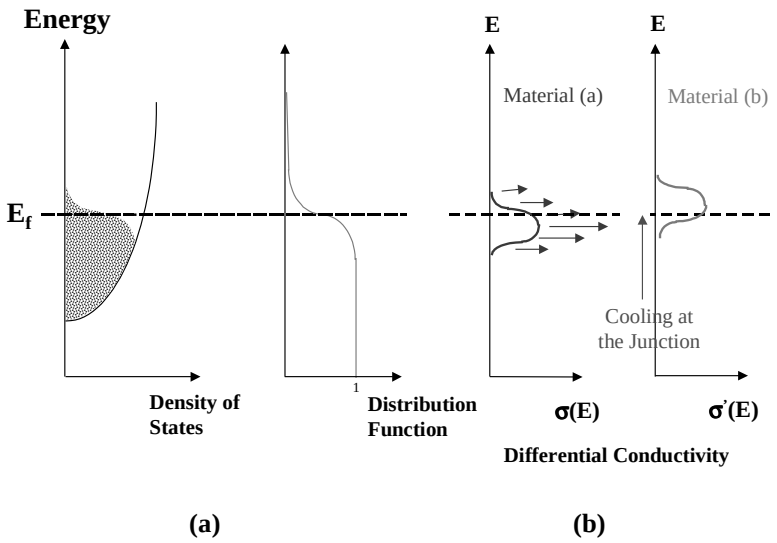

Fig. 1 (a) Density-of-states and Fermi distribution function versus energy for a degenerately doped n-type semiconductor. (b) The energy distribution of electrons moving in the semiconductor under an electric field is given by σ(E) the differential conductivity that determines the average transport energy of carriers. As the average transport energy increases from material "a" to material "b", thermal energy is absorbed from the lattice and the junction is cooled.

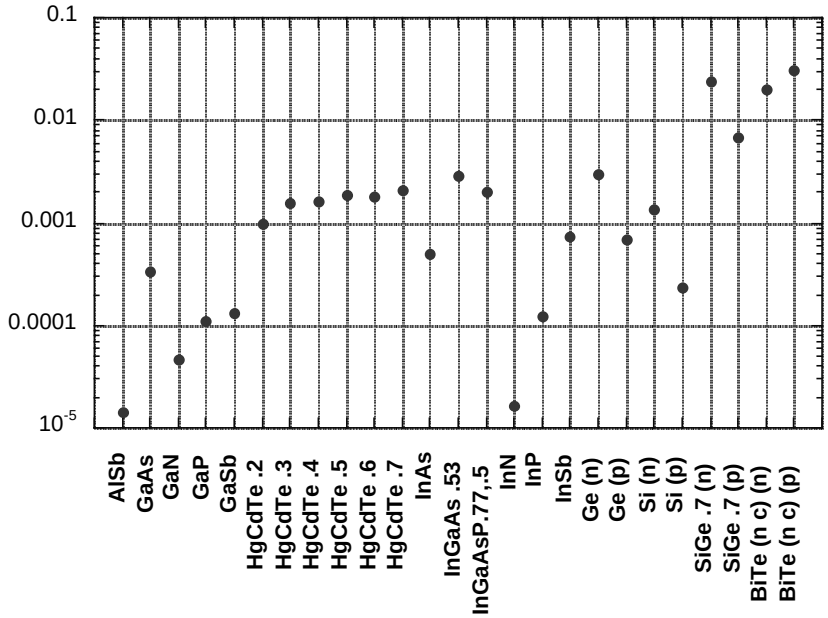

Fig. 2 The material parameter $\mu(m^*)^{1.5}/\beta$ for different compounds indicates the prospects of various semiconductors for thermionic or thermoelectric cooling. μ is the mobility in the barrier layer, β is the thermal conductivity and m* is the carrier effective mass.

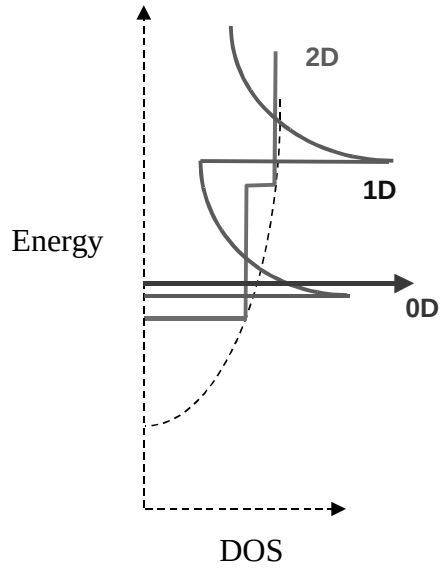

Fig. 3 The electronic density of states (DOS) versus energy for various dimensionalities (3D, 2D, 1D, and 0D). The first two quantified states are plotted.

energy transfer. In this case the requirement for symmetry in density of states can be relaxed (i.e. requirement for large electron effective mass), however one should consider additional effects due to scattering at the heterointerfaces. Due to the large surplus of electrons participating in conduction, smaller electric fields are needed to attain considerable cooling when compared with small barrier HIT coolers. Also this approximately ohmic conduction regime allows the electrical conductivity, Seebeck coefficient, and the Z parameter to be defined as in bulk material. An order of magnitude improvement in ZT has been predicted in multi barrier structures due to the dramatic increase in Seebeck coefficient [12]. This maximum ZT in multi barrier structures occurs for high doping densities where as in bulk material it happens at much lower doping densities. These calculations assumed bulk values for thermal conductivity of the multi layer films, however the actual thermal conductivity is expected to be lower for superlattices [16-18] resulting in further improvement of ZT.

Intuitive picture for low dimensional effects

From the previous discussion, the benefits associated with lower dimensional structures should be more apparent [19,20]. As the dimensionality is reduced, the electronic density of states accumulates near the subband transitions. With appropriate doping, step changes and even delta changes in available states for electrons would result in strong asymmetry in the differential conductivity and enhanced thermopower. Fig. 3 depicts the density of states versus energy in the 1D, 2D, and 3D regimes. Recently, Sofo and Mahan in a very nice paper have shown that the optimum transport distribution is a Dirac delta function centered about 2-3k_BT above or below the Fermi energy [21].

The advantages of heterostructure thermionic cooling can be combined with that of lower dimensional structures by using multi quantum well structures. The added constraint on the number of available electronic states would provide additional electron filtering and further improve the thermopower.

Conclusions

The material figure-of-merit for thermoelectrics had been shown to also describe prospective thermionic materials under certain approximations. The trade-off between electron effective mass and its mobility for thermoelectrics has been discussed, as well as the relaxation of the former requirement in high barrier thermionic emission cooling. The concept of differential conductivity was used and the importance of strong asymmetry was stressed. Achieving this large asymmetry was shown to be possible in thermionic emission over heterostructures, and further improvements for large barrier structures were presented. Finally an intuitive picture for the benefits of low dimensional effects was given using the argument of asymmetry in the differential conductivity. Heterostructure integrated thermionic coolers are expected to provide improved performance over conventional thermoelectric devices.

Acknowledgments

This work was supported by the Office of Naval Research and the Army Research Office through DARPA/HERETIC program.

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