Multilayer Thermionic Refrigeration

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A new method of refrigeration is proposed. Efficient cooling is obtained by thermionic emission of electrons over Schottky barriers between metals and semiconductors. Since the barriers have to be thin, each barrier can have only a small temperature difference ($\sim$1 K). Macroscopic cooling is obtained with a multilayer device. The same device is also an efficient generator of electrical power. A complete analytic theory is provided. [S0031-9007(98)05938-9]

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We provide the first detailed theoretical analysis of a new method of cooling which we call multilayer thermionic refrigeration. The same device can be used for power generation. We show that the expected efficiency is somewhere between one and two. This value is similar to freon-based refrigeration, and twice better than thermoelectric refrigeration [1,2]. The need to cool microelectronics, as well as to avoid the freon-ozone problem, has spurred the investigation of new methods of refrigeration.

Recently [3] one of us proposed a new method of refrigeration based on thermionic emission. For a device with a vacuum gap between parallel metal electrodes, room temperature refrigeration can be obtained with a work function less than 0.3 eV. This value is less than the work function for any known materials. Several groups have noted that such small barriers can be obtained in semiconductor multilayers [4–9]. In these cases, such as GaAs/AlAs, the barrier height can be adjusted by the alloying of Ga and Al in the Al_xGa_{1-x} barrier. We agree that this is viable geometry, although materials with low thermal conductivity such as PbTe would make better superlattices [10]. We also note that the Schottky barriers between some metals and semiconductors have barriers less than 0.1 eV [11,12]. In these cases, a device could be built which had alternate layers of metals and semiconductors, where the semiconductors are the barrier regions. Table I lists some typical systems with small barriers which could be used for multilayer thermionic refrigeration and power generation. Here we present a detailed analysis of the factors which make thermionic cooling viable in a multilayer geometry. This includes multiple quantum wells, as well as other periodic structures such as alternate layers of metal and semiconductors.

In thermionic emission, cooling is obtained when the thermally excited electrons escape over the barrier. Since hot electrons are leaving, the electrode cools. In equilibrium, electrons flow in both directions over the barrier, and there is no net cooling. Applying a voltage drives more electrons in one direction, and one electrode cools while the other heats up. It is a Peltier effect, but not a thermoelectric effect. The first idea is to have cooling by a single barrier. For example, in a three-layer sandwich consisting of metal-semiconductor-metal, the semiconductor is a barrier to the flow of electrons. We explain below why this idea does not work, and one is forced to go to the multilayer geometry. Then we analyze the properties of a system of N such barriers, consisting of a device of $2N + 1$ layers which are alternately metal and semiconductors. The same analysis also applies to periodic barriers formed from a superlattice of multiple semiconductor quantum wells when the current flow is perpendicular to the layers.

The reason for a multilayer device is that thermionic emission is the correct model only when the barrier thickness L is less than the mean-free path of the electron λ in the barrier. We wish to work in the regime where the electron can ballistically traverse the semiconductor barrier without scattering so that it does not diffuse.

On the other hand, if $L > \lambda$, then the electron flow through the semiconductor is described by the equation for the current due to drift and diffusion [13]. In this quasiequilibrium case, transport of heat is described by the thermoelectric equations. The heat currents in this case are smaller.

Since the barrier thickness L is small, then the ordinary heat flow $(-K\delta T/L)$ due to thermal conduction is going to be big for small L unless δT is also small. Since heat conduction lowers the efficiency, this conduction is reduced by insisting that δT is also small. Each thin barrier can permit only a small temperature difference.

TABLE I. Schottky barrier heights in eV, for various barriers and electrodes. $F(x)$ denotes values which are functions of x. The first two are metal-semiconductor superlattices, while the others are semiconductor superlattices.

Barrier	Electrode	$e\phi$	Ref.
$In_{0.7}Ga_{0.3}As$	Au	0.10	[11]
InSb	Au	0.10	[12]
$Eu_xPb_{1-x}Te$	PbTe	$F(x)$	[10]
Sb_2Te_3	Bi_2Te_3	0.035	[8]
Ge	Si	0.10	[8]

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A macroscopic temperature difference $\Delta T = N\delta T$ is achieved by having N barriers. Hence the need for the multilayer geometry. Adequate cooling power is available even for $\delta T_i \approx 1$ K. The energy current from thermionic emission is approximately given by $J_Q \approx AT\delta T\phi \exp(-e\phi/k_BT)$. With $A = 120$ A/(cm K)^2, $T = 260$ K, $\delta T = 1$ K, and $\phi = 0.05$ V, the prefactor of this expression is about 2 kW/cm^2. The exponential will reduce this by about a factor of 10, but there is ample energy current even for small temperature changes.

Another requirement for thermionic emission is that the electrons do not tunnel through the barrier. They must be thermally excited over the barrier. Electron tunneling through a square barrier of height $e\phi$ and width L has a probability with an exponent of $2L\sqrt{2m^* e\phi/\hbar^2}$. Thermionic emission has a probability with an exponent of $e\phi/k_BT$. For tunneling to be less important than thermionic emission, its exponent must be the largest. This gives the constraint $\lambda > L > L_t$ on the minimum thickness L_t

$$L_t = \frac{\hbar}{2k_BT}\sqrt{\frac{e\phi}{m^*}}\,. \tag{1}$$

These constraints are met easily. Most semiconductors with low barriers have narrow energy gaps, and therefore high mobilities. Typical numbers are that $L_t \sim 10$ nm while $\lambda \sim 100$ nm. There is a wide range of permissible barrier thicknesses. Also note that the tunneling and thermionic currents have different prefactors, which slightly alter the formula L_t. However, the above formula is a quick and reasonable estimate.

First, we solve for the currents over a single barrier. We assume the barrier is constant when the applied voltage is zero, but has the shape of a sawtooth with a nonzero voltage δV. The formulas for the electrical (J) and heat (J_Q) currents are given in Ref. [3] in terms of the hot and cold temperatures (T_h, T_c) and the applied voltage δV. We add to the heat current the thermal conduction $\delta T/R_1$ where R_1 is the thermal resistance of a single barrier. We now solve these equations for the case that the temperature difference $\delta T = T_h - T_c$ is small, and the voltage δV on a single barrier is small. We will show that for a single layer the optimal value of applied bias $e\delta V \propto \delta T$ which is also small. Denote as T the mean temperature of the layer, and then $T_c = T - \delta T/2$, $T_h = T + \delta T/2$. Then we expand the formulas for the currents in the small quantities ($\delta T/T, e\delta V/k_BT$) and get

$$J_R = AT^2 e^{-e\phi/k_BT}, \tag{2}$$

$$A = \frac{emk_B^2}{2\pi^2\hbar^3}\mathcal{T}\,, \tag{3}$$

$$J = \frac{eJ_R}{k_BT}[\delta V - V_J], \tag{4}$$

$$J_Q = J_R(b + 2)[\delta V - V_Q], \tag{5}$$

$$b = \frac{e\phi}{k_BT}\,, \tag{6}$$

$$eV_J = k_B\delta T[b + 2], \tag{7}$$

$$eV_Q = k_B\delta T\left[b + 2 + \frac{2 + Z}{b + 2}\right], \tag{8}$$

$$Z = \frac{e}{k_BR_1J_R} = Z_0e^b, \tag{9}$$

$$Z_0 = \frac{ek_B}{R_1A(k_BT)^2\mathcal{T}} = \left(\frac{T_R}{T}\right)^2, \tag{10}$$

$$(k_BT_R)^2 = \frac{2\pi^2\hbar^3}{mk_BR_1\mathcal{T}}\,. \tag{11}$$

Equation (2) is the standard Richardson's equation [13] for the thermionic current over a work function $e\phi$ which in this case is the Schottky barrier height between the metal and semiconductor. The factor of $\mathcal{T}$ denotes the fraction of electrons transmitted from the metal to the semiconductor. The formulas for J and J_Q assume the bias $e\delta V$ is to lower the Fermi level on the hot side, so that the net flow of electrons is from cold to hot. We have introduced the dimensionless constant Z_0 which plays an important role in the results. Refrigeration requires that $\delta V > V_Q$. High efficiency requires that $Z_0 < 4$. The dimensional constant T_R, which is determined by the thermal resistivity, should be less than about 500 K. For example, if $L = 50$ nm in a material with $K = 1.0$ W/(m K), then $R_1 = L/K = 5 \times 10^{-8}$ m^2 K/W and $T_R = 440$ K if m is an electron mass and $\mathcal{T} = 1$. Clearly this constraint limits the values of Z_0 and T_R which have acceptable efficiency. For larger values of Z_0 the effective efficiency becomes too small to be useful. As discussed in Refs. [14–18], the superlattice has a thermal resistance about 10 times larger than the resistance of the materials in it. The scattering from the interfaces gives a large thermal resistance [19,20]. This significant increase in the thermal resistance due to boundary scattering is an important aspect of getting high efficiency from the multilayer thermionic device.

Now consider the theory of the multilayer thermionic refrigerator. We assume N barriers, with alternate electrodes. Denote δT_i and δV_i to be the temperature and voltage changes across one barrier. These values change substantially from the initial to the final layer. This change is due to the generation and flow of heat. At each barrier, the electron ballistically crosses the barrier region, and then loses an amount of energy $e\delta V_i$ in the electrode. The heat generated at each electrode must flow out of the sample according to the equation

$$\frac{d}{dx}(J_{Qi}) = J\frac{\delta V_i}{L_i}\,, \tag{12}$$

where L_i is the effective width of one barrier plus one metal electrode. We take L_i to be a constant, although it could vary with i. The device thickness is $D = NL_i$. We assume that the functions change slowly with i and we can treat them as continuous variables dT/dx and dV/dx.

These are not thermoelectric devices. However, it is useful to examine the analogy with thermoelectric devices. Once we linearize the equations for small voltage drops, and then make them continuous in a multilayer geometry, they are identical in form to the equations of a thermoelectric. This analogy is obtained with the relationships for the conductivity σ, the Seebeck coefficient S, and the thermal conductivity K.

$$\sigma = \frac{eJ_R L_i}{k_B T}, \tag{13}$$

$$S = \frac{k_B}{e}(b + 2), \tag{14}$$

$$K = \left(2\frac{k_B}{e}J_R + \frac{1}{R_1}\right)L_i, \tag{15}$$

$$Z = \frac{\sigma S^2 T}{K} = \frac{(b + 2)^2}{(2 + z)}. \tag{16}$$

The first term in the thermal conductivity is the electronic contribution K_e. The last line gives the dimensionless figure of merit Z. It is known in thermoelectric devices that one wants to have Z to be as large as possible. Varying b to maximize Z gives the relationship

$$be^b = 4\left(\frac{\overline{T}}{T_R}\right)^2, \tag{17}$$

where $\overline{T}$ is the mean temperature in the device. We find this to be an accurate estimate of the optimal barrier height ϕ. Furthermore, the thermoelectric estimates of the efficiency of the refrigerator (η_r) and generator (η_g),

$$\eta_r = \frac{\gamma T_c - T_h}{\Delta T(\gamma + 1)}, \tag{18}$$

$$\eta_g = \frac{\Delta T(\gamma - 1)}{\gamma T_h + T_c}, \tag{19}$$

$$\gamma = \sqrt{1 + Z}, \tag{20}$$

are remarkably accurate compared to the computer solutions. In thermoelectric devices it is rare to have values of Z to be larger than one. However, in modeling thermionic devices we find values of Z much larger than one for reasonable values of thermal resistance. The efficiencies of the thermionic devices are correspondingly much higher than in thermoelectric devices. Ballistic transport carries more heat than diffusive flow.

We have solved numerically Eqs. (4), (5), and (12) using the methods in Ref. [21]. Figure 1 shows the numerical results for a refrigerator with $T_c = 260$, $T_h = 300$, and several values of T_R. This calculation was done for $N = 40$, but any large value of N gives the same result. These results should be compared to the efficiencies of a freon compressor ($\eta \approx 1.4$) and a thermoelectric module ($\eta \approx 0.7$). The present devices have a higher efficiency. We have run many cases of cooling with different parameters. The computer predicts that one can even cool over a temperature difference of $\Delta T = 100$ from room temperature. We also find that the estimate (18) is accurate to about 1%.

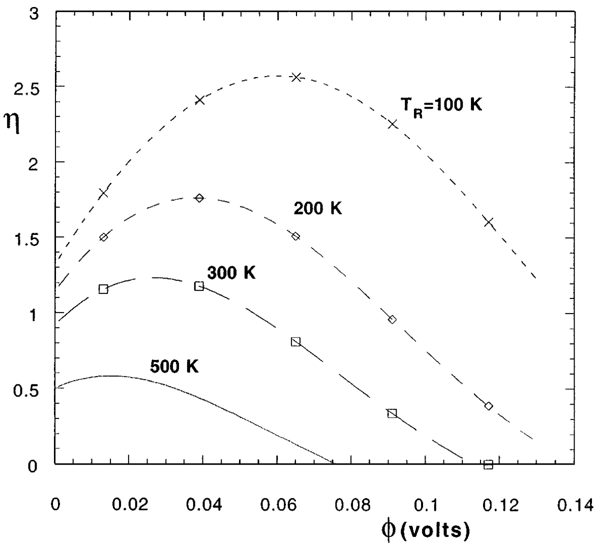

FIG. 1. The efficiency η of a refrigerator, with $T_c = 260$ K and $T_h = 300$ K, as a function of barrier height ϕ for several values of T_R. Results are higher than for a thermoelectric refrigerator which has $\eta = 0.70$ when $ZT = 1$.

The same equations apply to the calculation of the power generator. Then the electrons flow from hot to cold. Equations (4), (5), and (12) still apply but now J and J_Q are negative. We compare the efficiency of the generator to those of thermoelectric devices with a dimensionless figure of merit $ZT = 1$. If $T_c = 300$ K and $T_h = 400$ K, the thermoelectric generator has an efficiency of $\eta = 0.048$. Two sets of results are given for thermionic devices ("TI") corresponding to $T_R = 200$ K ($\eta = 0.099$) and $T_R = 400$ K ($\eta = 0.065$). The thermionic device with $T_R = 200$ K has twice the efficiency of a thermoelectric one for the same range of temperature difference. It is interesting that increasing T_R by a factor of 2 has only a small change in the efficiency. This is equivalent to a factor of 4 change in the thermal resistance. The optimal barrier height ϕ shifts downward in value as T_R is increased, and partly compensates for the change in thermal resistance.

The cooling power of this device may already have been demonstrated. In Ref. [8] the authors report significant cooling along the c axis in a multilayer device. They explain this behavior as due to an increased thermoelectric effect, and interpret it as an increase in the Seebeck coefficient. Their barrier layers are so thin that we suggest they are observing thermionic emission rather than increased thermoelectricity. For their device with superlattice constant 200 Å we estimate $R_1 = 16 \times 10^{-8}$ m^2 K/W which gives $T_R = 246$ K.

We have prepared a longer manuscript [22] where these ideas are discussed at greater length.

In summary, we announce the invention of a new method of refrigeration and power generation based on multilayer thermionic emission. We show that this device could have an efficiency which is twice that of present thermoelectric devices. The efficiency of the refrigerator is similar to that of freon-based compressors. The present devices have no moving parts, and should last forever. They have no adverse environmental impacts.

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