Enhanced Thermionic Emission Cooling in High Barrier Superlattice Heterostructures

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ABSTRACT

Thermionic emission current in heterostructures can be used to enhance thermoelectric properties beyond what can be achieved with conventional bulk materials. The Bandgap discontinuity at the junction between two materials is used to selectively emit hot electrons over a barrier layer from cathode to anode. This evaporative cooling can be optimized at various temperatures by adjusting the barrier height and thickness. Theoretical and experimental results for nonisothermal thermionic emission in heterostructures are presented. Single stage InGaAsP-based heterostructure integrated thermionic (HIT) coolers are fabricated and characterized. Cooling on the order of a degree over one micron thick barriers has been observed. Nonisothermal transport in highly doped tall barrier superlattices is also investigated. An order of magnitude improvement in cooling efficiency is predicted for InAlAs/InP superlattices.

INTRODUCTION

Current state-of-the-art thermoelectric material for cooling and energy conversion at room temperature is based on BiTe. This material was discovered in 1950's. Its thermoelectric figure-of-merit ZT ($=S^2\sigma T/\beta$) is about 0.7-0.9. This corresponds to efficiencies on the order of 7-10% of Carnot efficiency [1-3]. This is much smaller than the efficiency of compressor based refrigerators that is more than 40-50%. Hence, conventional thermoelectrics have had limited applications for low cooling powers (< 50W) [4]. Various factors contribute to the low efficiency of thermoelectric refrigerators. Vining in a recent article [5] gave a lucid description of the thermoelectric process and pointed out a major difference with gas-cycle engines, i.e. the absence of phase transition near operating temperatures. A recent and important application of thermoelectric coolers is for temperature stabilization of optoelectronic components (lasers, filters, switches, etc.) used in high speed and wavelength division multiplexed fiber optics communication systems. In this case, the important factors are cost, reliability, and size [6]. Efficiency is not the major issue.

Thermionic emission in heterostructures was recently proposed as a mean to increase the *cooling power* of conventional semiconductor materials such as AlGaAs, InGaAsP, HgCdTe or SiGe beyond what can be achieved with bulk thermoelectrics [7-8]. In thermionic emission process, hot electrons from a cathode layer are selectively emitted over a barrier to the anode junction. Since the energy distribution of emitted electrons is almost exclusively on one side of Fermi energy, upon the current flow, strong carrier-carrier and carrier-lattice scatterings tend to restore the quasi-equilibrium Fermi distribution in the cathode by absorbing energy form the lattice, and thus cooling the emitter junction. The performance of the device can be optimized at

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various temperatures and for different cooling powers by changing the height and thickness of the barrier layer.

In the following we will review the initial theoretical predictions and experimental results for single barrier heterostructure integrated thermionic (HIT) coolers. After discussing some of the practical difficulties to achieve optimum performance of these thin film devices, we extend our analysis to highly doped structures. We will first describe the conventional trade off between electrical conductivity and Seebeck coefficient in bulk materials. Tall barrier HIT coolers are then proposed as a mean to overcome this trade off. It is shown that with proper doping one can increase the *efficiency* of InGaAs/InAlAs HIT coolers by as much as an order of magnitude with respect to the bulk material.

SMALL BARRIER HIT COOLERS

A schematic diagram of a single barrier HIT cooler as proposed in Ref. [7] is shown in Fig. 1. Thermionic emission is well understood in semiconductors, and is used in many devices. The hottest electrons are emitted over a barrier and collected on the other side. The coolest electrons remain behind. Vacuum thermionic generators were intensively studied in the 1950's and 60's [11,12]. They convert the heat energy into electricity by extracting electrons from hot metal plates onto another cold plate. The same device could work as a cooler by reversing the direction of current, but this cooler can only work at very high temperatures (>700°C) due to the availability of low work function metals and because the current flow is limited by space charge between the plates [13]. Thinner gaps work better, but there are limits to how close two plates can be placed to each other. Uneven gaps result in highly nonuniform current flow and hot spots develop.

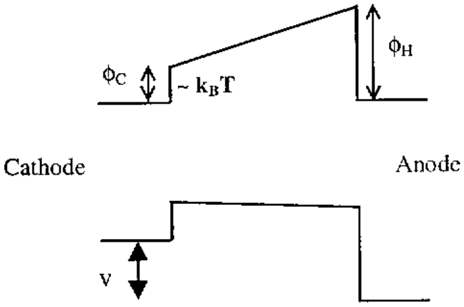


Fig. 1 Small barrier heterostructure integrated thermionic emission for high cooling power densities at room temperature.

The precise control of layer thickness and composition using techniques of molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition (MOCVD), in conjunction with bandgap engineering allow the design of *semiconductor* thermionic emission devices with improved cooling capacities. One can easily design different barrier heights in the anode and in the cathode (typically 0 to 0.4eV). This is determined by the bandedge discontinuity between heterolayers. Depending on the growth constraints and lattice mismatch between materials, one can grade the barrier composition to produce internal fields and to enhance electron transport properties (see Fig. 1). Close and uniform spacing of cathode and anode is not a problem anymore and is achieved with atomic resolution.

Theoretical predictions

The overall cooling capacity of a single barrier HIT cooler, with cathode side barrier height of ϕ_C, barrier thickness d and its thermal conductivity β, can be expressed as

$$Q_{TI} = \left[\Phi_C + 2\frac{k_B T_C}{e}\right]\cdot I \\ - IV\left[\left(\frac{1}{2} - \frac{\lambda_E}{d}\right) - \frac{{\lambda_E}^2}{d^2}\left(e^{-d/\lambda_E} - 1\right)\right] - \frac{\beta}{d}\Delta T$$

where k_B is the Boltzmann constant, e the electric charge, T_C the cold side (cathode) temperature, and $\Delta T = T_H - T_C$. λ_E is the energy relaxation length for carriers [8]. The dependence on electrical conductivity of the barrier (carrier mobility) is hidden in the I(V) relationship [8]. This energy balance equation has three terms that describe thermionic cooling at the cathode, "Joule" heating in the barrier and heat conduction from the hot to the cold side. Thermionic cooling is equal to average energy of emitted electrons time the current. Assuming Boltzmann distribution for carriers, which is valid for barrier heights > $2k_BT$, this average energy is $(\phi_C + 2k_BT_C/e)$. The Joule heating term is IV times a coefficient, which takes into account the finite electronic energy relaxation length λ_E. In the limit of very thick devices, this coefficient reduces to 1/2 which is the result for pure diffusive transport. In the other limit of very short devices, the Joule heating term vanishes. In this case of ballistic transport, all of the electron's energy is deposited at the anode side.

In order to optimize HIT cooling devices, it is important to minimize Joule heating in the barrier. It is thus necessary to understand what are the main mechanisms that determine electronic energy relaxation length (λ_E) in semiconductors. For this purpose we will use Monte Carlo simulations of electron transport in GaAs. Other III-V semiconductors such as InP have similar characteristics. Ternary and quartenary compounds have in addition alloy scattering, but this is not expected to change energy relaxation considerably.

Fig. 2 displays the Joule heating as a function of distance for 5000 electrons injected over a 0.1 eV barrier into a 3 μm thick GaAs layer under an electric field of 5 kV/cm. It can be seen that, it will take about 1 μm before electrons reach equilibrium and lose energy equal to what they gain at steady state from the external electric field. Fig. 2 displays also the contribution of major scattering processes to electron energy relaxation as a function of distance. It can be seen that major scattering events responsible for energy relaxation at short distances (< 0.5μm) are polar optical phonon emission and absorption in the Gamma valley. At longer distances, there is a substantial population in the L valley. In this case, L-valley polar optical phonon emission and absorption and inter L-valley scatterings will start to contribute to the electronic energy loss mechanisms.

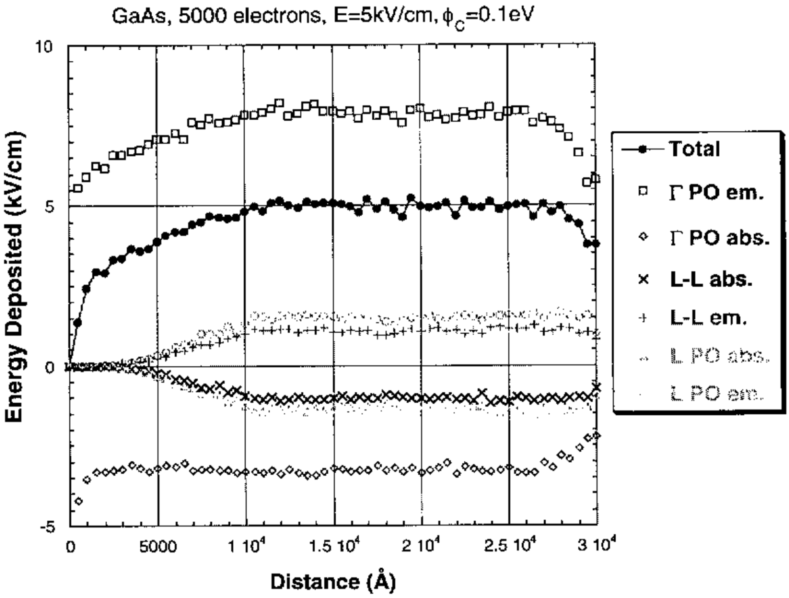


Fig. 2 Monte Carlo simulation of Joule heating as a function of distance for 5000 electrons injected over a 0.1 eV barrier into a 3-micron thick GaAs layer. Various curves show different energy loss mechanisms in a thin barrier heterostructure device. The important processes are Γ-valley polar optical phonon (PO) emission and absorption, L-valley PO phonon scattering and inter L-valley scattering (L-L).

Using various material parameters of InGaAs, and taking 0.4 μm for energy relaxation length, we can calculate the net cooling power at the cold side as a function of the thickness of the barrier for different cathode barrier heights (Fig. 3). The anode barrier height does not enter directly in the calculation of maximum cooling power. It is assumed to be high enough to suppress the reverse current form the hot to the cold side. It can be seen that at room temperature, thermionic cooling can maintain a temperature gradient of 10 degrees over a distance of 2 microns and provide a net cooling power of couple of 100 W/cm^2. The currents required for this cooling are on the order of 50 kA/cm^2.

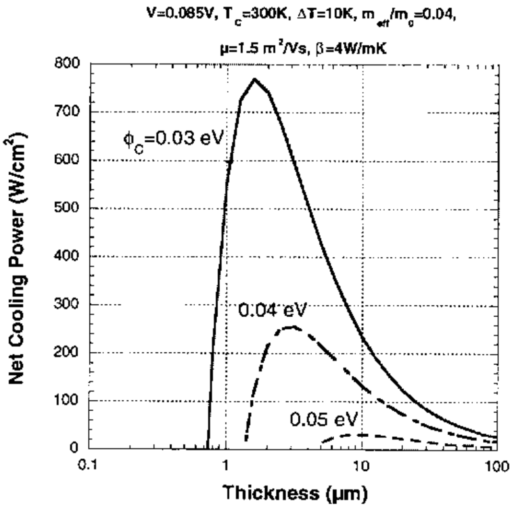


Fig. 3 Calculated net cooling power as a function of barrier thickness for small barrier InGaAs HIT cooler. Different curves correspond to different cathode side barrier heights.

Experimental results

In order to investigate experimentally thermionic emission cooling in heterostructures, a single InGaAsP (λ_{gap}=1.3 μm) barrier surrounded by n^+ InGaAs cathode and anode layers was grown using metal organic vapor phase epitaxy (MOCVD). Cathode and anode layer thicknesses were 0.3 and 0.5 μm and they were doped to $3x10^{18}$ cm^{-3}. The barrier layer had an n-doping of $2x10^{17}$ cm^{-3} and was one micron thick. Mesas with an area of 90x180 μm^2 were etched down using dry etching techniques. Ni/AuGe/Ni/Au was used for top and bottom contact metallization. Fig. 4a displays the temperature on top and on the bottom of the device as well as the substrate temperature far away from the device as a function of current. All temperatures are relative to the value at zero current. The rise in substrate temperature is an indication of the relatively high thermal resistance of ceramic package and the soldering layer used to mount the sample. Despite the poor performance of the heat sink on the anode side, a net cooling of 0.5°C is observed on top of the device. This cooling over 1 μm thick barrier corresponds to cooling capacities on the order of 200-300 W/cm^2. To understand these results a two dimensional finite difference heat equation solver (ANSYS) was used to simulate the performance of the device. Joule heating in the layers, substrate, and gold wire bonds were included as well as thermionic emission cooling (heating) at the cathode (anode) junction and the thermoelectric effect at the metal/semiconductor junctions. The Peltier effect at the junction InGaAs(n^+)/Au was studied by applying current between two bottom contacts. A cooling 2-3 times smaller than the thermionic cooling was measured.

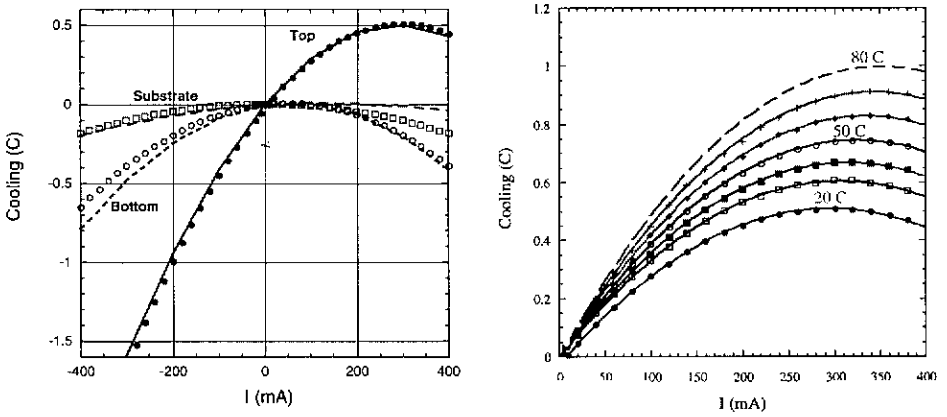


Fig. 4 (a) Measured temperature on top and on the bottom of the HIT cooler, as well as the substrate temperature far away form the device as a function of current. All temperatures are relative to the value at zero current. The heat sink temperature is 20°C. The simulation results are solid curve for top temperature, short-dashed curve for bottom temperature and dashed curve for the substrate. (b) Measured cooling at various substrate (heat sink) temperatures.

Assuming the thermal conductivity of InGaAsP to be 2 W/mK (i.e. 50% of textbook value [17]) and a solder layer and package with total thermal resistance of $2.5\text{x}10^3$ K/W, the overall cooling and the temperature distribution in the device fit reasonably well the measured values in Fig. 4a. The simulation results are solid curve for top temperature, short-dashed curve for bottom temperature and dashed curve for the substrate. In order to minimize the effect of series and contact resistances, a number of p- and n-type HIT coolers connected electrically in series and thermally in parallel should be used (similar to conventional thermoelectric cooling modules). By improving the packaging, 10°C cooling for single stage InGaAsP HIT coolers is expected.

Fig. 4b displays the measured cooling at various substrate temperatures. The device cools much better at higher temperatures. A net cooling of about 1°C is measured at 80°C. The reason for the improved performance is two fold. First, the thermal conductivity of the barrier decreases at higher temperatures, and second, thermionic emission cooling increases due to the larger thermal spread of carriers near the Fermi energy.

The above theoretical and experimental results indicate the potential of HIT devices to achieve high cooling power densities. These devices have, however, a low efficiency (a few % of the Carnot value). The main problem is that the high cooling power at the cathode should fight the large heat flux that is coming from the hot junction only 1 or 2 μm away. As it can be seen in Fig. 3, the device can not achieve net cooling when the barrier is thick. For the case of thick barriers, electron transport is not any more determined by the "supply" of electrons at the cathode. One thus loses the advantages of thermionic emission cooling. Recently Mahan et al. [15-16] have proposed to use multi barrier thermionic coolers to achieve ZT's a factor of 2-3 better than the bulk values. Their design is based on small barrier heights (~ k_BT), and uses the ballistic transport of electrons in very thin superlattice barriers.

Based on a different approach, in the following we first briefly reexamine the trade off between high electrical conductivity and large Seebeck coefficient in bulk semiconductors. We will then introduce tall barrier HIT coolers, as a mean to overcome this trade off. Preliminary theoretical analysis of InGaAs/InP and InGaAs/InAlAs superlattices HIT coolers show that an improvement in efficiency by an order of magnitude with respect to the bulk material can be achieved.

ELECTRICAL CONDUCTIVITY AND POWER FACTOR TRADE OFF IN BULK THERMOELECTRICS

In the conventional thermoelectric effect, electrons flow from a material in which they have an average transport energy smaller than the Fermi energy to another material in which their average transport energy is higher. They thus absorb thermal energy from the lattice and this will cool down the junction between two materials. In Fig. 5(a) we can see that at high doping densities there are many more carriers that contribute to the conduction process. Despite the reduction in electron mobility due to charged impurity scattering, the net electrical conductivity continues to rise with doping concentration.

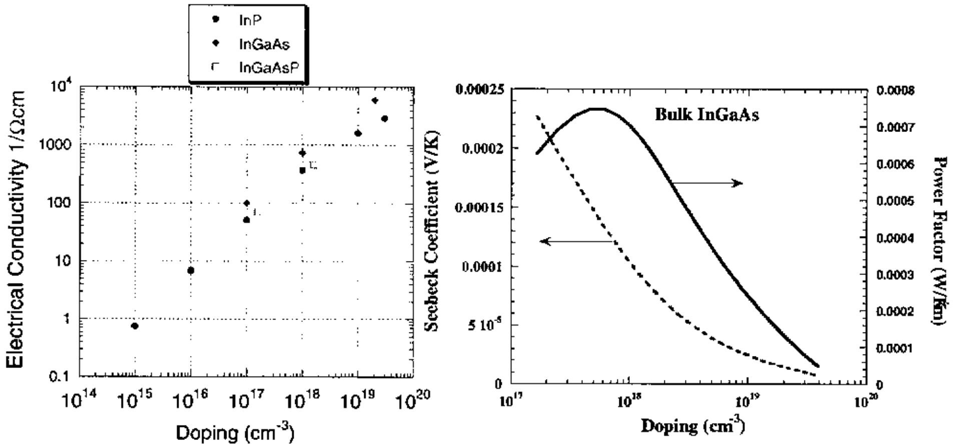


Fig. 5 (a) Experimental electrical conductivity of InP, InGaAs, InGaAsP (λ_{gap}=1.3 μm) as a function of doping. (b) Substantial decrease in Seebeck coefficient at high dopings is the cause of low power factor and thus poor ZT.

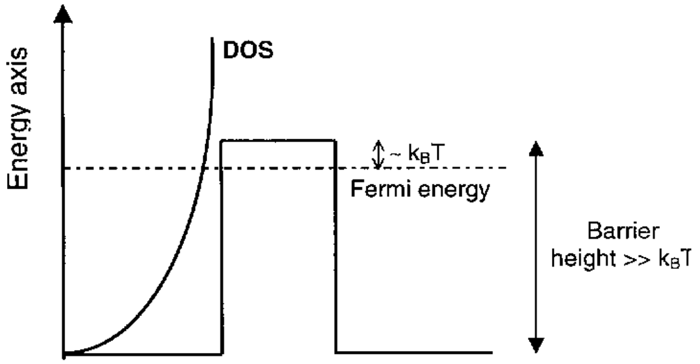
Fig. 5(b) shows that the poor power factor (electrical conductivity times square of Seebeck coefficient) is a result of significant decrease in Seebeck coefficient when Fermi energy is deep inside the conduction band. At high doping densities, the situation is similar to the metals. Since the Fermi energy is deep inside the band, there are almost as many electrons above the Fermi energy as the ones below, so the average energy of moving electron gas under an electric field is very close to the Fermi level. This gives a small thermopower (Seebeck coefficient), and thus poor thermoelectric cooling properties.

High barrier heterostructure integrated thermionic coolers

Tall barriers in a highly degenerate semiconductor can be used to selectively emit hot electrons, and to achieve thermionic emission cooling similar to the original small barrier HIT coolers. Because of the large number of electrons involved in the conduction process, small electric fields can be applied to achieve substantial cooling. In this near ohmic conduction regime, electrical conductivity, Seebeck coefficient and the Z parameter can be defined similar to bulk material.

Fig. 6 displays the thermoelectric figure-of-merit for bulk InGaAs as a function of doping. The experimental doping dependence of electron mobility is included in the calculations. This figure shows also the expected ZT for multibarrier structures with tall InP ($\Delta Ec=0.24$ eV) or InAlAs ($\Delta Ec=0.51$ eV) barriers. The order of magnitude improvement in ZT is due to large increase in Seebeck coefficient at high doping densities in multibarrier devices. The thermal conductivity of the composite material is taken to be 5 W/mK, i.e. identical to the bulk InGaAs. Several recent studies [18-20] have shown that superlattice thermal conductivity is also reduced comparing to bulk value, so further improvement in ZT is expected.

In the above analysis quasi diffusive transport of electrons above the barriers is assumed. We do not expect significant changes in the device performance due to the finite electron energy relaxation length. In fact, corrections due to ballistic transport will tend to improve the cooling characteristics even more.



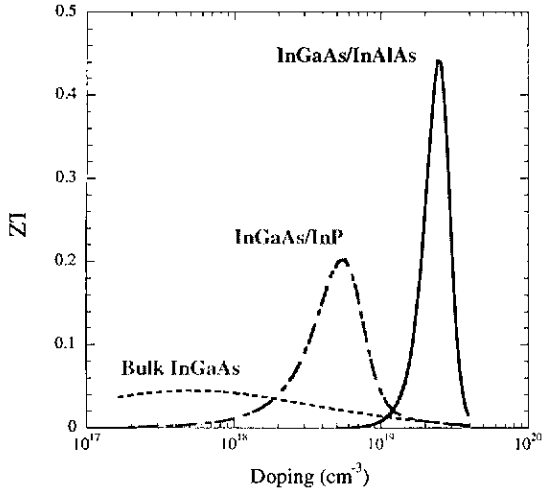


Fig. 6 Theoretical thermoelectric figure-of-merit (ZT) for bulk InGaAs and for high barrier heterostructure thermionic coolers based on InGaAs/InP (ΔE_c=0.24eV) and InGaAs/AlGaAs (ΔE_c=0.51eV) at various doping densities. The thermal conductivity of the composite material is taken to be 5 W/mK, i.e. identical to the bulk value. The order-of-magnitude improvement in ZT is purely due to thermionic emission of hot carriers above the barrier.

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REFERENCES

1. H. J. Goldsmit, *Electronic Refrigeration* (Pion, London, 1986).

2. D. M. Rowe, *CRC Handbook of Thermoelectrics* (CRC Press, New York, 1995).

3. C. B. Vining, Thermoelectric materials of the future, in Twelfth International Conference on Thermoelectrics, Yokohama, 1993, P. 126.

4. H. B. Lyon Jr., Overview of industrial interest in new thermoelectric materials, in *Thermoelectric Materials - New Directions and Approaches*, Materials Research Society, Symposium Proceedings vol. 478, Ed. T. M. Tritt et al., P. 285-296, 1997.

5. C. B. Vining, The thermoelectric process, in *Thermoelectric Materials - New Directions and Approaches*, Materials Research Society, Proc. vol. 478, Ed. T. M. Tritt et al., P. 3-13, 1997.

6. L. Rushing, A. Shakouri, P. Abraham, and J. E. Bowers, Micro thermoelectric coolers for integrated applications, in the proceedings of Sixteen International Conference on Thermoelectrics, Dresden, Germany, August 1997.

7. A. Shakouri, J. E. Bowers, Heterostructure integrated thermionic coolers, Appl. Phys. Lett. 71, 1234 (1997).

8. A. Shakouri, E. Y. Lee, D. L. Smith, V. Narayanamurti, J. E. Bowers, Thermoelectric effects in submicron heterostructure barriers, Microscale Thermophysical Engineering 2, 37 (1998).

9. D. M. Rowe, and G. Min, Multiple potential barriers as a possible mechanism to increase the Seebeck coefficient and electrical power factor, in Thirteen International Conference on Thermoelectrics, Kansas City, pp. 339-342, 1994.

10. L. W. Whitlow, and T. Hirano, Superlattice applications to thermoelectricity, Journal of Applied Physics, vol.78, pp. 5460-5466, 1995.

11. B. Moyzhes, Possible ways for efficiency improvement of thermoelectric materials, in Fifteenth International Conference on Thermoelectrics, Pasadena, 1996, P. 183.

12. G. N. Hatsopoulos, E. P. Gyftopoulos, *Thermionic energy conversion* (Vol. I, II) (Cambridge, MIT Press 1973-79).

13. G. D. Mahan, Thermionic refrigeration, J. of Appl. Phys., 1 Oct. 1994, vol.76, (7), P. 4362.

14. A. Shakouri, C. LaBounty, J. Piprek, P. Abraham, J. E. Bowers, Thermionic emission cooling in single barrier heterostructures, Appl. Phys. Lett. (to be published January 1999).

15. G. D. Mahan, L. M. Woods, Multilayer thermionic refrigeration, Phys. Rev. Lett. 80, 4016 (1998).

16. G. D. Mahan, J. O. Sofo, M. Bartkowiak, Multilayer thermionic refrigerator and generator, J. Appl. Phys. 83, 4683 (1998).

17. S. Adachi, *Properties of InP* (INSPEC, UK, 1993).

18. D. G. Cahill, Heat transport in dielectric thin films and at solid-solid interfaces, Microscale Thermophysical Engineering, vol.1, pp. 85-110, 1997.

19. G. Chen, Thermal conductivity and ballistic-phonon transport in the cross-plane direction of superlattices. Phys. Rev. B (Condensed Matter), vol.57, pp.14958-73, 1998.

20. R. Venkatasubramanian, E. Siivola, T. S. Colpitts, In-plane thermoelectric properties of freesstanding Si/Ge superlattice structures, in Seventeenth International Conference on Thermoelectrics, Nagoya, Japan, 1998.