Thermal, electrical and thermoelectric transport in nanostructured ErAs:InGaAlAs materials

A. Shakouri*, Z. Bian, R. Singh, M. Zebarjadi, Y. Ezzahri, Y. Zhang, D. Vashaee[1]
Baskin School of Engineering
University of California at Santa Cruz, USA

J. M. Zide[2], G. Zeng, J-H. Bahk, H. Lu, D. O. Klenov, J. LeBeau,
S. Stemmer, A. C. Gossard and J. E. Bowers
Materials Department, Electrical and Computer Engineering
University of California at Santa Barbara, USA

W. Kim[3], S. Singer and A. Majumdar
Mechanical Engineering Department
University of California at Berkeley, USA

P. M. Mayer and R. J. Ram
Research Laboratory of Electronics
Massachusetts Institute of Technology, USA

V. Rawat and T. D. Sands
Material Science and Engineering
Purdue University, USA

K.J. Russel and V. Narayanamurti
School of Engineering and Applied Sciences
Harvard University, USA

*ali@soe.ucsc.edu
Current addresses: [1]Oklahoma State University, USA;
[2]University of Delaware, USA; [3]Yonsei University, Korea

Abstract
After a brief comparison of thermoelectric and solid-state thermionic effects, we describe a novel thermo-electric material based on semimetallic ErAs nanoparticles in a semiconductor InGaAlAs matrix. Hot electron filtering using heterostructure barriers is used to break the trade off between high Seebeck coefficient and high electrical conductivity. In addition, the embedded nanoparticles reduce the lattice thermal conductivity by scattering long and medium wavelength phonons. As the atomic periodicity and the arsenic sublattice are not disturbed, electron mobility is comparable to that of bulk InGaAlAs crystal. ErAs nanoparticles provide free carriers. The electron concentration is tripled when temperature is increased from 300 to 600K. Energy selective electron scattering by nanoparticles is crucial to explain the increase in Seebeck coefficient in the same temperature range. Measurement of the thermal conductivity, electrical conductivity and Seebeck coefficient show that a ZT of about 1 is achieved at 600 K. Integrated circuit fabrication techniques are used to transfer the n- and p-type 10 or 20 microns thick thin films onto AlN plates and 400 elements power generation modules are fabricated. An output power density ~2.5W/cm^2 is demonstrated at a temperature difference of 120 K across the module.

Introduction
Energy consumption in our society is increasing rapidly. A significant fraction of the energy that is generated is lost in the form of heat. Direct thermal to electrical energy conversion systems that could operate at lower temperatures (300-650C) with high efficiencies (>15-20%) provide an attractive compact alternative to internal combustion engines. They will also expand the possibilities for waste heat recovery applications. An average ZT of 1.5 in the whole temperature range is needed in order to reach these goals.

Thermoelectric and solid-state thermionic energy conversion

The idea of thermionic energy conversion was first seriously explored in the mid fifties during the development of vacuum diodes and triodes. Vacuum diode thermionic refrigerator was proposed by Mahan [1] in 1994. He predicted very high efficiencies, but the device could only work at high temperatures (>700K) due to the lack of low workfunction materials and due to the space charge potential in the millimeter size vacuum gaps. In early to mid 1990's several groups pointed out the advantage of electron energy filters in bulk thermoelectric materials [2,3,4]. A factor of 2 or so improvement in ZT was predicted; however these papers were not widely referenced. To overcome the limitations of vacuum thermionics at lower temperatures, thermionic emission cooling in heterostructures was proposed by Shakouri and Bowers [5] In these structures, a potential barrier is used for selective emission of hot electrons and evaporative cooling of the electron gas. The thermionic cooler can be based on a single barrier or a multi barrier structure. In a single barrier structure in the *ballistic* transport regime, which is strongly *nonlinear*, electric current is dominated by the supply of electrons in the cathode layer. Large cooling power densities can be achieved if optimum barrier height and thickness are chosen and if the anode is in contact with an ideal heat sink [5]. However, the energy conversion efficiency in these structures is low. The ballistically emitted electrons release all of their excess energy in the anode and produce significant heating. In general, in order to approach the Carnot limit, the transport should be quasi-reversible and near equilibrium.

On the other hand, for a multi barrier structure at small biases, the transport is linear and one can define an effective Seebeck coefficient and electrical conductivity. Mahan and Woods [6] were first to linearize the conventional Richardson equation for the thermionic emission current in a multibarrier device. Their initial calculations suggested that multibarrier structures can have efficiencies twice as large as conventional thermoelectrics [6]. However more detailed analysis by Radtke et al. [7], Ulrich et al. [8] and Mahan and Vining [9] showed that linearized Richardson equation does not produce electronic efficiencies higher than thermoelectrics and it was claimed that the only benefit of the multilayer structure is in reducing the lattice thermal conductivity [10]. These calculations don't give the full potential of multibarrier devices since the focus was only on small barrier heights (conduction band discontinuity on the order of the thermal energy) and also because authors used the linearized version of the Richardson equation which is not a good approximation when the Fermi energy is near the barrier height. For a more accurate analysis of the electron transport perpendicular to superlattice layers, a modified Boltzmann transport equation was proposed that takes into account the quantum mechanical transmission through barriers [11]. This model explained very well the measured dark current of multiquantum well structures used in infrared detector applications in a wide range of temperatures [12].

The motivation to work on *metal*-based superlattices and embedded nanoparticles was based on the theoretical calculation of Vashaee and Shakouri [11,12] who predicted ZT>5 is possible for optimized structures even with a lattice contribution to thermal conductivity on the order of 1W/mK. The main idea is that *in a thermoelectric energy conversion device, work is extracted from the random thermal motion of electrons*, so in principle we would like to have *as many electrons as possible in the material*. However, highly degenerate semiconductors and metals are not good bulk thermoelectric materials due to their low Seebeck coefficient. In reference [13], authors analyzed the trade off between electrical conductivity and the Seebeck coefficient and explained that highly degenerate semiconductors and metallic structures can have high thermoelectric power factors (Seebeck coefficient square times electrical conductivity) if there is an appropriate *hot electron filter* (*potential barrier*) that selectively scatters cold electrons. In fact, highly efficient *tall* barrier metallic superlattices were first suggested in 1998 [14], however detailed modeling of electron transport in these structures revealed the importance of *lateral momentum non-conservation* [15]. The basic idea is that planar superlattices are *momentum filters* and not *energy filters* [16]. Only hot electrons with a large enough kinetic energy in the direction perpendicular to barriers are transmitted, while lots of other *hot* electrons are blocked. In order to achieve non-conversation of lateral momentum in the thermionic emission process, one can break the translation invariance in the plane of the superlattice by adding roughness or one could use 3D potential barriers [17,18]. An intriguing paper by Meshkov [19] suggested that electron-electron interaction when coupled to other scattering mechanisms can couple in-plane and out-of-plane degrees of freedom. He predicted that the electron tunneling rate through a planar barrier will be governed by the total energy of electrons (rather than the kinetic energy in the direction perpendicular to the barrier). However, the implications of this work on electron transport in superlattices are still under investigation [11,12,20].

Potential metal/semiconductor heterostructure systems

The theoretical analysis presented earlier showed the potential of metal-based hot-electron filters. Many metals can be grown epitaxially on top of semiconductors, however growth of high quality semiconductors on top of metals is difficult. There are not many candidate systems for high quality, high-electron-mobility, metal/semiconductor composites. Authors, who are members of the Thermionic Energy Conversion Center [28], concentrate on two material systems: the first one is the rare-earth based III-V semiconductors (such as ErAs:InGaAlAs) and the second one is the nitride-based metal/semiconductor multilayers (such as TiN/GaN [21]). In this paper, we focus on the first material system.

InGaAlAs embedded with ErAs nanoparticles

ErAs is a rocksalt semimetal which can form into epitaxial nanometer-sized particles on an III-V semiconductor surface. Overgrowth is nucleated on the exposed semiconductor surface between the particles and is essentially defect-free. The properties of the resulting nanocomposite are dependent on the composition of the host semiconductor and on particle morphology, which can be controlled during growth. For thermoelectric applications, we concentrated on the incorporation of ErAs into various compositions of InGaAlAs (lattice matched to InP). The particles pin the Fermi level at an energy that is dependent both on the particle size and the composition of the semiconductor. For example, the Fermi level of InGaAs is pinned within the conduction band, increasing the free electron concentration and thus the electrical conductivity. We first focused on developing structures which consisted of superlattices of ErAs islands in an InGaAs matrix, which was lattice matched to an InP substrate. To maintain a constant ErAs concentration our initial samples consisted of ErAs depositions ranging from 0.05 monolayers/period to 0.4 monolayers/period, with the superlattice period varying from 5 nm to 40 nm. While InGaAs is not a good thermoelectric materials to start with (room temperature ZT ~ 0.05), the incorporation of ErAs reduced the thermal conductivity of the material by approximately a factor of 2 (i.e., total thermal conductivity ~4W/mK) [22]. At the same time, in-plane measurements of the Hall effect showed an increased carrier concentration for smaller particles and a high-quality material with mobilities of 2000-4000 cm^2/Vs at 300K [23]. We then concentrated on the growth of co-deposited (randomly distributed) ErAs:InGaAs, which has the advantage of growing much faster than superlattice structures because it does not require growth interrupts (see Fig. 1). This allows us to grow much thicker structures with greater stability. Our initial efforts focused on 0.3% ErAs, which is the same concentration as the initial superlattice samples. The Hall effect and Seebeck measurements have shown that these materials are electrically very similar to the superlattice materials with a thermoelectric power factor (Seebeck square tirnes electrical conductivity) similar to bulk InGaAs [23]. On the other hand, the thermal conductivity was reduced by 25% compared to the ErAs/InGaAs superlattice material [22]. The significant reduction compared to bulk alloy material (a factor of 2.5-3) is due to the increased scattering of mid- to long- wavelength phonons by embedded nanoparticles. This makes this system one of the only materials in which thermal conductivity is reduced below the so-called "alloy limit" without creating defects that lower electron mobility and electrical conductivity. Kim et al. have recently developed a detailed model for phonon transport in these structures, and the simulated lattice thermal conductivity matches well the experimental result over a wide temperature range [24].

In order to increase the number of carriers participating in transport and improve the thermoelectric power factor, we studied n-type ErAs:InGaAs structures with InGaAlAs barriers for electron filtering. These barriers actually consist of a short-period superlattice or "digital alloy" of InGaAs and InAlAs. By carefully choosing the composition of the InGaAlAs/InGaAs multilayers, we can create electron filtering barriers to improve the thermoelectric power factor at a given temperature. The cross-plane thermoelectric transport properties were measured using mesa structures with integrated thin film heaters/sensors. Experimental results confirmed the increase in the cross-plane Seebeck coefficient by a factor of three compared to the in-plane value [25,26].

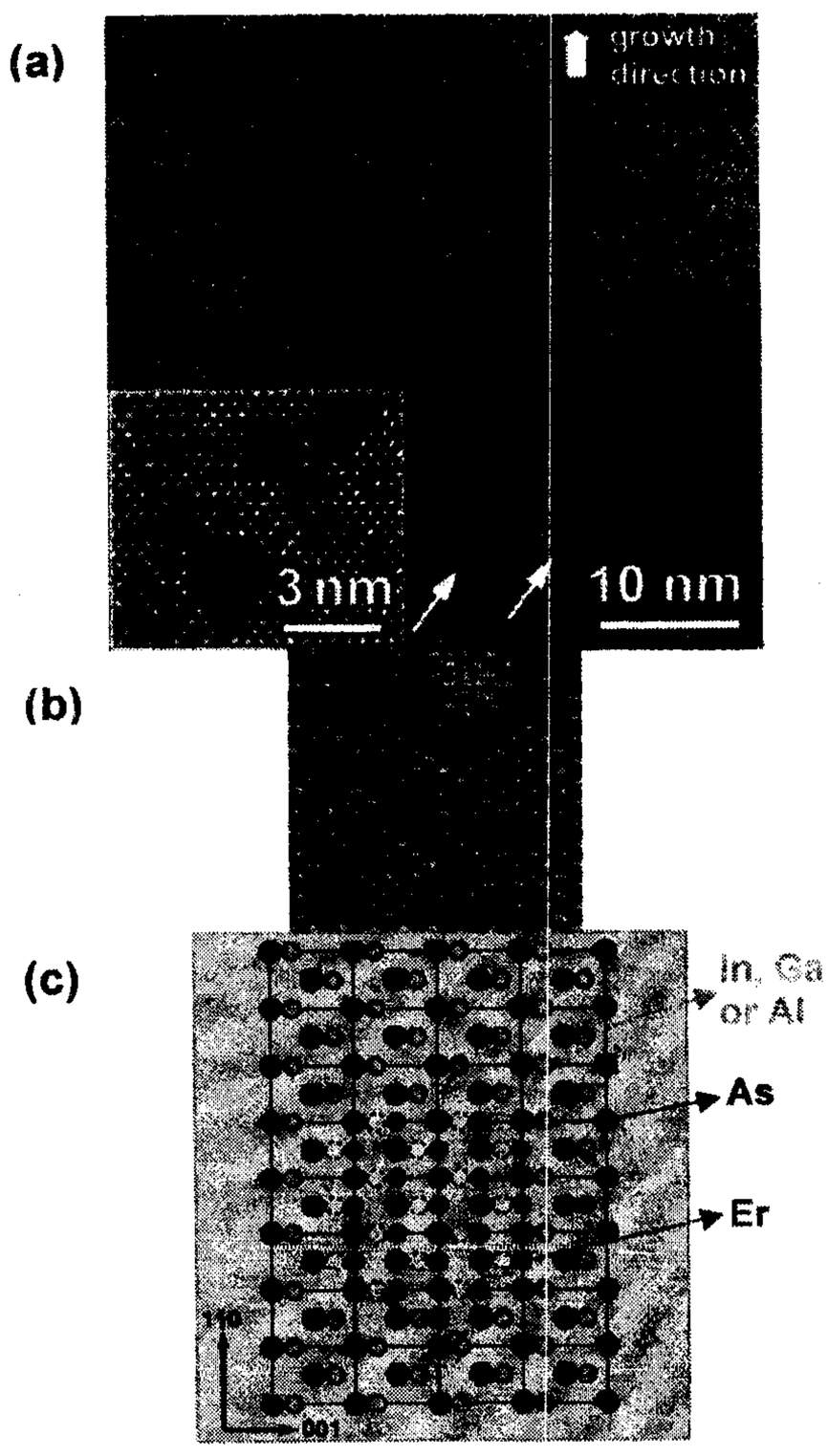

Fig. 1 (a) Transmission electron micrograph of InGaAs matrix with randomly-distributed ErAs nanoparticles. (b) high-angle annular dark-field imaging in scanning transmission electron microscopy and (c) the crystal structure showing that arsenic sub-lattice is continuous throughout ErAs/InGaAs nanocomposite.

Recently, we have focused on the incorporation of ErAs into InGaAlAs alloy. The main idea suggested by Joshua Zide was that the Fermi-level pinning at the interface of ErAs/InGaAlAs can be used to create 3D Schottky potential barriers which can selectively scatter hot electrons. This can create a solid-state thermionic device without the use of superlattice barriers. As the material is isotropic, the

measurement of the transport properties is much easier. The differential 3ω method was used to measure the thermal conductivity of InGaAlAs (20% Al) embedded with 0.3% ErAs nanoparticles. In Fig. 2 (a), the measured thermal conductivity versus temperature is shown. The thermal conductivity decreases with temperature and the fitting curve is very close to a straight line in the temperature range between 300 K and 600 K. The thermal conductivity of ErAs-InGaAlAs (20% Al) is much lower than that of bulk InGaAlAs and very close to that of ErAs:InGaAs.

The electrical conductivity of 0.5 μm thick ErAs:InGaAlAs (20% Al) grown on insulating InP substrate was measured using the Van der Pauw method (see Fig. 2(b)). The electrical conductivity increases with temperature. This is because the number of free electrons thermally excited out of ErAs particles increases with temperature by almost a factor of 3. This was verified by the Hall measurements by Thierry Caillat at JPL.

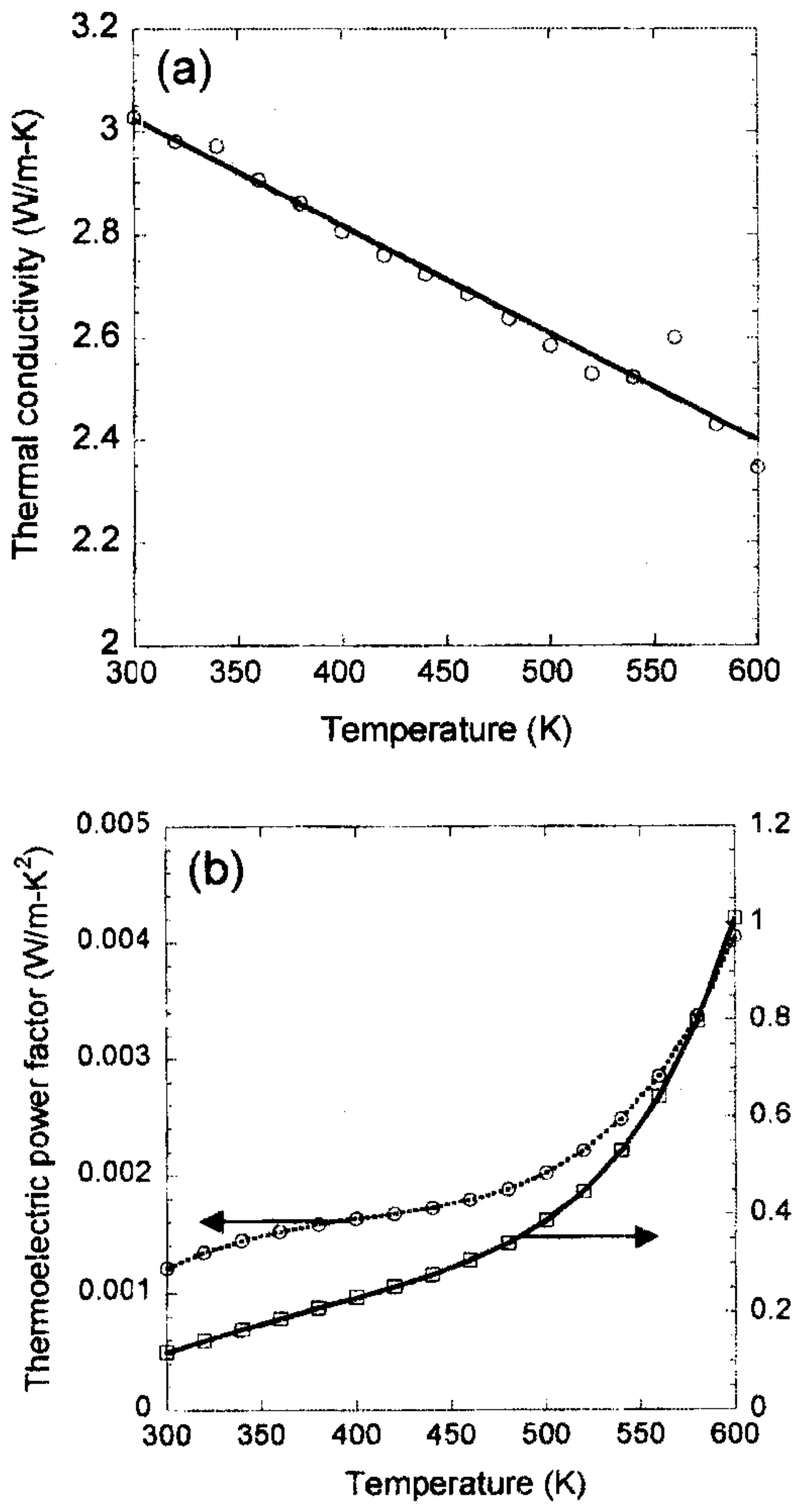

Fig. 2 (a) Thermal conductivity (b) power factor and ZT of InGaAlAs (20% Al) embedded with 0.3% ErAs nanoparticles versus temperature.

It is very interesting to see that all three parameters: thermal conductivity, electrical conductivity, and Seebeck coefficient, go to the favored direction of having a larger ZT when the temperature increases. This is not usual for bulk materials and it is due to ErAs nanoparticles and their hetero-interfaces with the InGaAlAs alloy. The Thermoelectric power factor and figure-of-merit ZT are calculated from the three independently measured parameters and are plotted in Fig. 2 (b). ZT~1 is achieved at 600K. Further measurements are underway to study ZT at higher temperatures. The material seems to be stable at temperatures as high as 800K. However electrical measurements are affected by the electrical conductivity of the intrinsic InP substrate at higher temperatures. We are working on the characterization of thin film only devices where the substrate is removed.

Thin film modules

To generate large enough open circuit voltage, many n-type and p-type thermoelectric elements need to be connected electrically in series and thermally in parallel. We used InGaAlAs alloys embedded with ErAs nanoparticles. The n-type had 20% Aluminum and it was not intentionally doped. All of the free electrons came from ErAs nanoparticles. The p-type leg had 0% Aluminum concentration (e.g. it was InGaAs) and it was doped with Be to reach a free hole concentration of $5x10^{19}$ cm^{-3}. Wafer scale processing and flip-chip bonding were used to fabricate multi element thin film power generation module. Both n- and p-type InGaAlAs thin films grown on InP substrate were patterned to a 200 elements array. Each element had a cross sectional area of 120×120 μm^2. The element mesas were formed using inductive coupling plasma dry etching. The n- and p- element arrays were flip-chip bonded to the gold plated AlN substrate. After removing the InP substrate by selective wet etching, the two AlN plates are flip-chip bonded together to form a power generation module. The detailed fabrication process can be found in Ref. [27].

Modules with 10 or 20 microns thick thin films were made. It is also very important to optimize the heat sink so that a large temperature drop can be obtained across the active legs. In this measurement, the heat sink was made of copper with forced cooling water. The generator module was placed on the heat sink and heat was applied to the top surface through a copper bar. Thermocouples were used to measure the temperature drop across the generator module. The open circuit voltage was 2.1 and 3.5V for modules with 10 and 20 micron tall elements, respectively. The corresponding external temperature drop was 120 K. Then variable external load resistances were used to extract the output power. The maximum output power per unit area of the active element was 1- 2.5 W/cm^2, respectively (see Fig. 3).

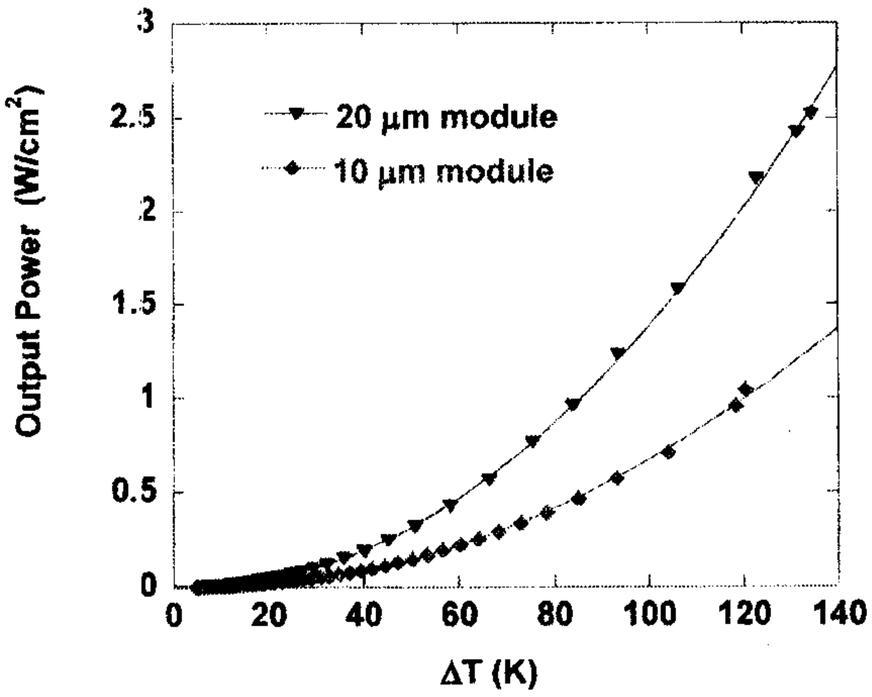

Fig. 3. The output power density versus temperature difference for 400 element, 10 and 20 microns thick ErAs:InGaAlAs power generator module.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research through MURI Thermionic Energy Conversion Center program [28] managed by Dr. Mihal Gross. Authors would like to acknowledge Dr. Thierry Caillat at NASA Jet Propulsion Laboratory for high temperature Hall measurements.

REFERENCES:

[1] G.D. Mahan, "Thermionic Refrigeration," J. Applied Physics, 76, pp. 4362-4366, 1994.

[2] B. Ya. Moyzhes and V. A. Nemchinsky, Report on the XI International Conference on Thermoelectrics, IEEE, Arlington, TX, pp. 232–235, 1992; B. Moyzhes, Possible ways for efficiency improvement of thermoelectric materials, in Fifteenth International Conference on Thermoelectrics, Pasadena, P. 183, 1996.

[3] 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.

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

[5] Shakouri, A. and J.E. Bowers, "Heterostructure Integrated Thermionic Coolers," Applied Physics Letters, 71, pp. 1234-1236, 1997.

[6] G.D. Mahan, and L.M. Woods, Phys. Rev. Lett. 80, 4016 (1998).

[7] R.J. Radtke, H. Ehrenreich, and C.H. Grein, J. Applied Physics 86, 3195 (1999).

[8] M. D. Ulrich and P. A. Barnes and C. B. Vining, "Comparison of solid-state thermionic refrigeration with thermoelectric refrigeration,"Journal of Applied Physics, vol. 90, no 3, pp. 1625-1631, 2001

[9] G.D. Mahan, and C.B. Vining, J. Appl. Phys. 86, 6852 (1999).

[10] G.S. Nolas, J.W. Sharp and H.J. Goldsmid, Thermoelectrics: Basics Principles and New Materials Developments, Springer-Verlag, 2001.

[11] D. Vashaee, A. Shakouri, "Improved Thermoelectric Power Factor in Metal-Based Superlattices" Physical Review Letter, Vol.92, no. 10, pp. 106103-1, 2004.

[12] D. Vashaee, A. Shakouri. Electronic and thermoelectric transport in semiconductor and metallic superlattices. Journal of Applied Physics, vol.95, no.3, pp.1233-45, 2004.

[13] A. Shakouri, "Thermoelectric, thermionic and thermophotovoltaic energy conversion" International Conference on Thermoelectrics, Clemson, NC, , pp. 492-497, 2005.

[14] Ali Shakouri, Chris Labounty, Patrick Abraham, Joachim Piprek, and John E. Bowers, "Enhanced thermionic emission cooling in high barrier superlattice heterostructures", Material Research Society Symposium Proceedings, Vol. 545, pp.449-458, December 1998.

[15] D. Vashaee, A. Shakouri, Conservation of lateral momentum in heterostructure integrated thermionic coolers. Thermoelectric Materials 2001 - Research and Applications. Symposium (Materials Research Society Symposium Proceedings Vol.691). Mater. Res. Soc., pp.131-45. Warrendale, PA, USA, 2001.

[16] T. E. Humphrey and M. F. O'Dwyer, "A Comparison Between Solid-state Thermionics and Thermoelectrics," Journal of Applied Physics 98, 026108, 2005.

[17] T.E. Humphrey and H. Linke, "Power Optimisation of Thermionic Devices" J. Phys. D. 38 2051 (2005).

[18] Zhixi Bian and Ali Shakouri, "Enhanced solid-state thermionic emission in non-planar heterostructures," Appl. Phys. Lett. 88, pp 0121021-3, 2 Jan. 2006.

[19] S. V. Meshkov, Sov. Phys. JETP 64, 1337 (1986).

[20] K.J. Russel and V. Narayanamurti (private communications); see also: K.J. Russell, Ian Appelbaum, V. Narayanmurti, M.P. Hanson, and A.C. Gossard, Transverse momentum nonconservation at the ErAs/GaAs interface, Phys. Rev. B 71, 121311(R) (2005).

[21] V. Rawat and T. Sands, "Growth of TiN/GaN Metal/Semiconductor Multilayers by Reactive Pulsed Laser Deposition, J. Appl. Phys. 100, 064901(2006); V. Rawat and T. Sands TiN/GaN Metal/Semiconductor Multilayer Nanocomposites Grown by Reactive Pulsed Laser Deposition, MRS Proc. Vol 872, pp. J21.4.1-6 (2005).

[22] Kim, W., Singer, S., Majumdar, A., Zide, J., Gossard, A., and Shakouri, A., 2005, "Role of nanostructures in reducing thermal conductivity below alloy limit in

crystalline solids," The 24th International Conference on Thermoelectrics, pp. 9-12.

[23] J. M. Zide, D. O. Klenov, S. Stemmer, A. C. Gossard, G. Zeng, J. E. Bowers, D. Vashaee and A. Shakouri, "Thermoelectric power factor in semiconductors with buried epitaxial semimetallic nanoparticles", Applied Physics Letters , 87 , pp.112102-1-3, September, 2005.

[24] W. Kim, S. Singer, A. Majumdar, D. Vashaee, Z. Bian, A. Shakouri, G. Zeng, J. E. Bowers, J. M. O. Zide, A. C. Gossard, Appl. Phys. Lett., **88**, 242107 (2006).

[25] Gehong Zeng, Zide JMO, Woochul Kim, Bowers JE, Gossard AC, Zhixi Bian, Yan Zhang, Shakouri A, Singer SL, Majumdar A. , "Cross-plane Seebeck coefficient of ErAs:InGaAs/InGaAlAs superlattices", Journal of Applied Physics, vol.101, no.3, pp. 34502-1-5, 1 Feb. 2007.

[26] J. M. Zide, D. Vashaee, G. Zeng, J. E. Bowers, A. Shakouri, A. C. Gossard, Demonstration of electron filtering to increase the Seebeck coefficient in ErAs:InGaAs/InGaAlAs superlattices, vol.74, no.20, , pp. 205335-1-5, 15 Nov. 2006.

[27] G. Zeng, J. E. Bowers, J. M. O. Zide, A. C. Gossard, W. Kim, S. Singer, A. Majumdar, R. Singh, Z. Bian, Y. Zhang, and A. Shakouri, "ErAs:InGaAs/InGaAlAs superlattice thin-film power generator array", Applied Physics Letters 88, pp 113502-1-3, 13 March, 2006.

[28] A. Shakouri et al., "Solid-State and Vacuum Thermionic Energy Conversion," Proceedings of the Material Research Society, Fall Meeting, Boston, MA, December, 2005.