Thermoelectricity:
From Atoms to Systems

Week 5: Recent Advances in Thermoelectric Materials and Physics

Lecture 5.1: Thermionics vs. Thermoelectrics

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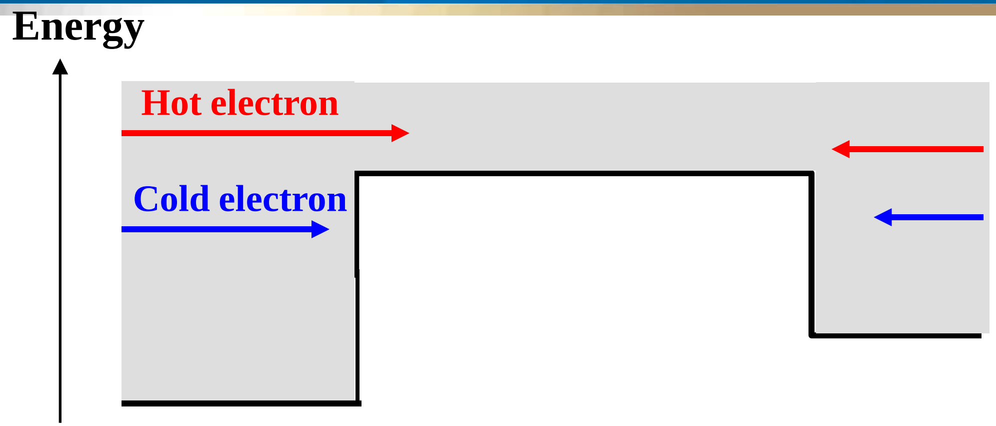
Vacuum vs. Solid-State Thermionic Emission



	Cathode	Barrier	Anode
Vacuum	Low work function	Vacuum (ions)	Low work function

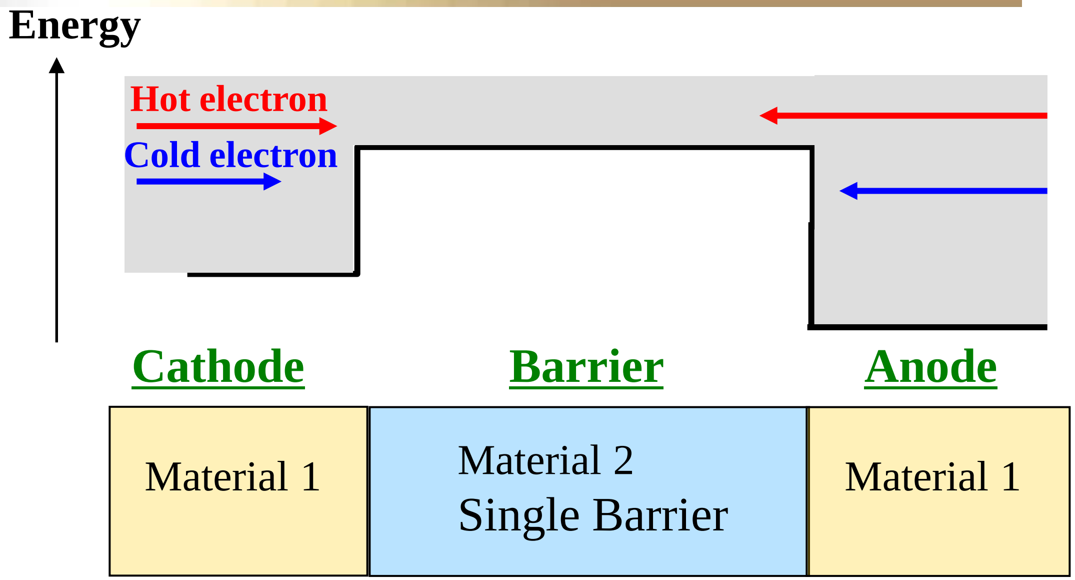
1950-60's for space power generation (Hastapoulous); G.D. Mahan suggested for cooling (1994)

Solid-State	Metal/ Deg. Semicond	Solid-State Barrier	Metal/ Deg. Semicond

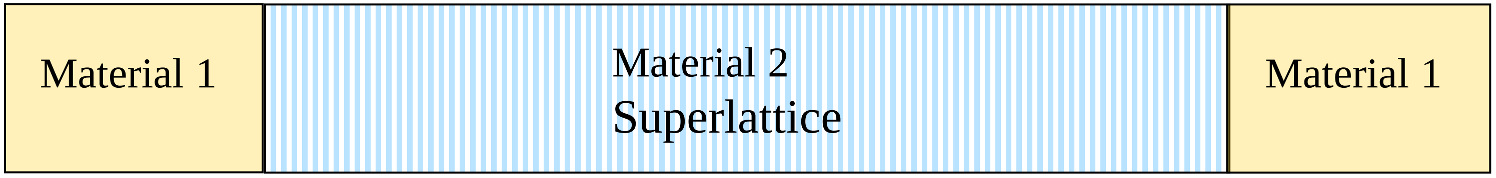
Shakouri and Bowers, Appl. Phys. Lett. (1997) –Single barrier device, non-linear regime
Mahan et al. Phys. Rev. Lett. (1998) – Multi barrier device, linear transport regime

- Selective emission of hot electrons over a potential barrier can cool the emitter by evaporative cooling
- Thermodynamic reverse process: temperature difference creates voltage

Thermionic (TI) vs. Thermoelectric (TE)

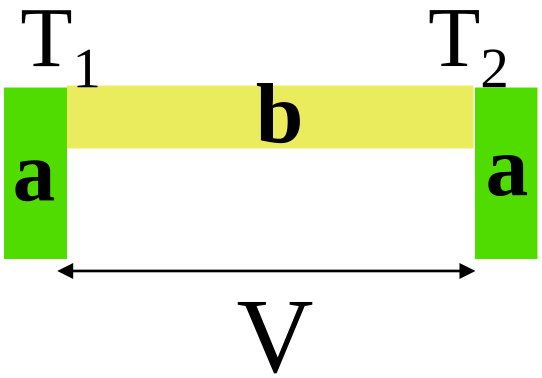


Thermionic: If barrier is thin (< electron energy relaxation length) => Can not define barrier Seebeck coef. independent of contact layers (ballistic, non-linear transport)



Superlattice: In linear transport regime can define an "**effective**" Seebeck coefficient for the superlattice (linearized TI=TE)

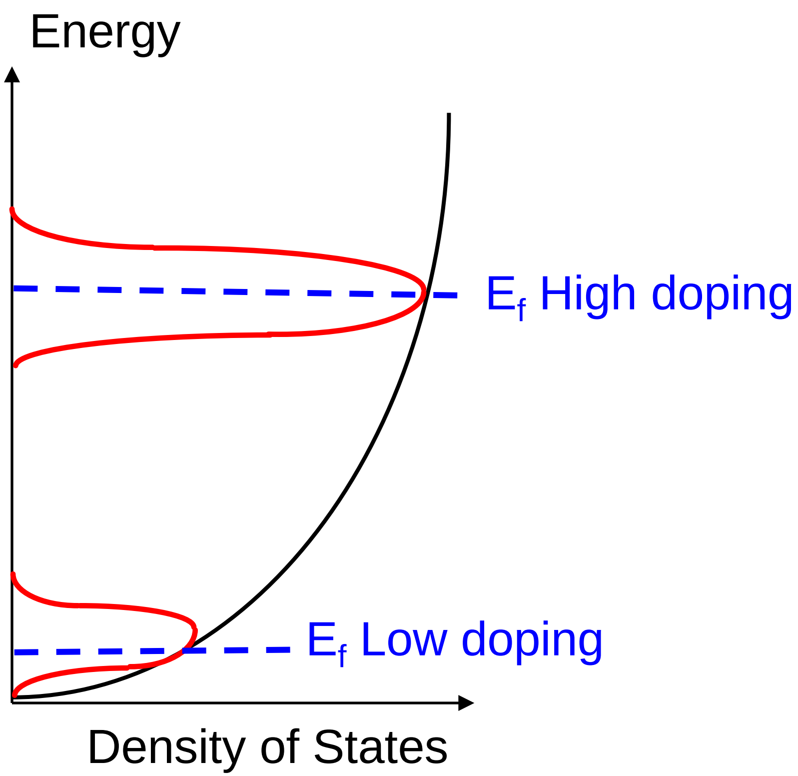
- Thermoelectric:
  - Bulk property (manifested at interfaces),
  - Linear transport
  - Nonlinear TE in bipolar devices or high currents (Pipe, Ram & Shakouri '02; Zebarjadi et al. '07)

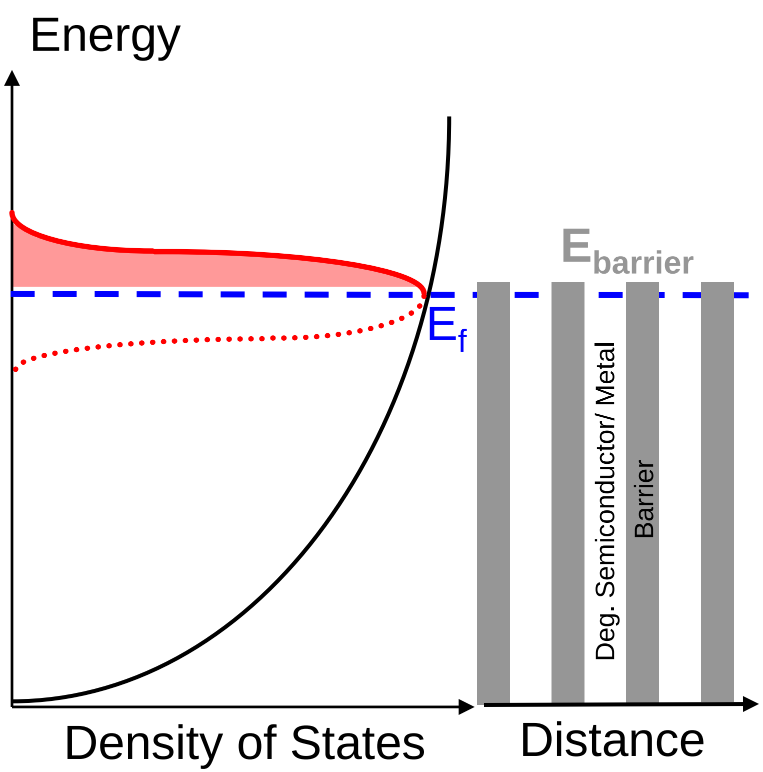


Solid-State Thermionics vs. Thermoelectics

- Solid-State Thermionic
  - Interface effect
  - Single barrier non-linear transport ⇒ High Cooling Power Density (Shakouri & Bowers '97; Shakouri, Lee, Smith, Narayanamurti & Bowers '98)
  - Multiple barrier ballistic transport ⇒ High Efficiency (β↓) (Mahan '98, Ulrich `01)
  - Tall barrier superlattice in linear transport (Shakouri & Bowers '99)
  - InP and SiGe -based thin film coolers (Bowers, Shakouri, Majumdar, Narayanamurti, Croke) Cooling>500 W/cm^2 demonstrated
  - Metallic/Semiconductor superlattice (Vashaee & Shakouri PRL'04, T. Sands et al. '08) ONR, MURI TEC Center '03-10/DARPA NMP

Seebeck –Conductivity Trade off





Doped Bulk Semiconductor

Deg. Semiconductor/Metal + Energy Filter (Thermionic emission)

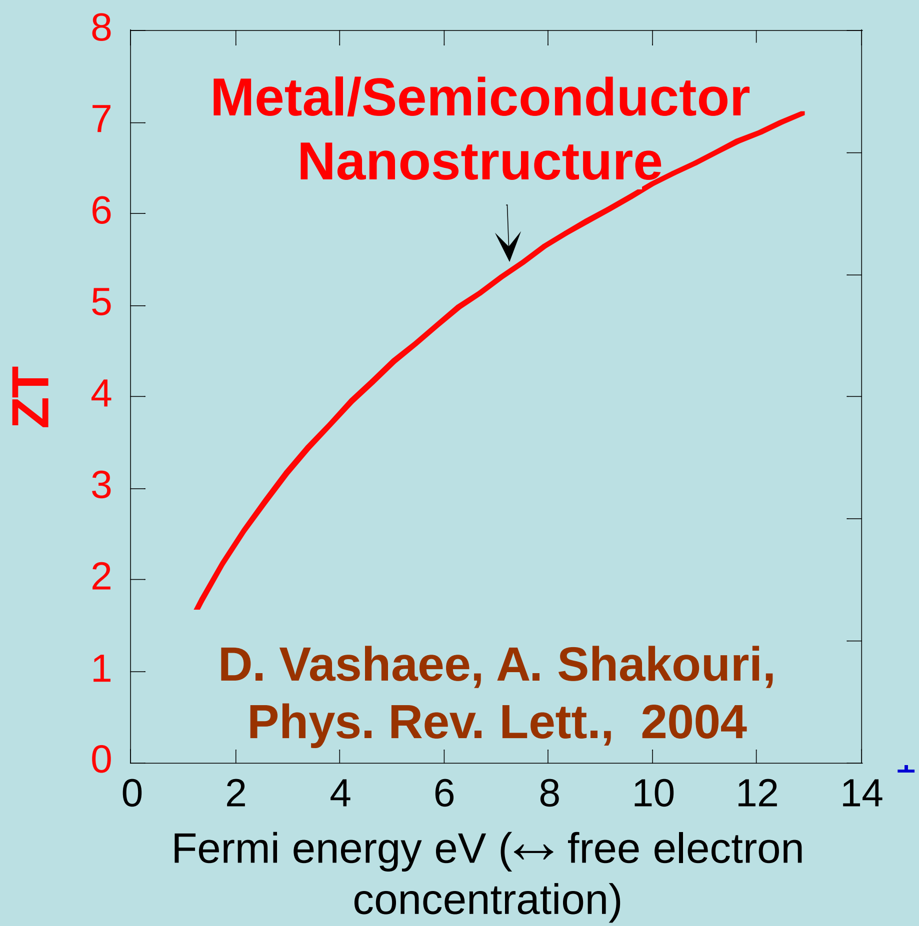
Symmetry of DOS near Fermi energy is the main factor determining Seebeck coefficient.

A. Shakouri, "Thermoelectric, thermionic and thermophotovoltaic energy conversion", ICT 2005

Thermionic Energy Conversion Center

Even with only modestly low lattice thermal conductivity and electron mobility of typical metals, ZT > 5 is possible with hot electron filters.

Assume: $\kappa_{lattice}$=1W/mK, mobility ~10 cm^2/Vs

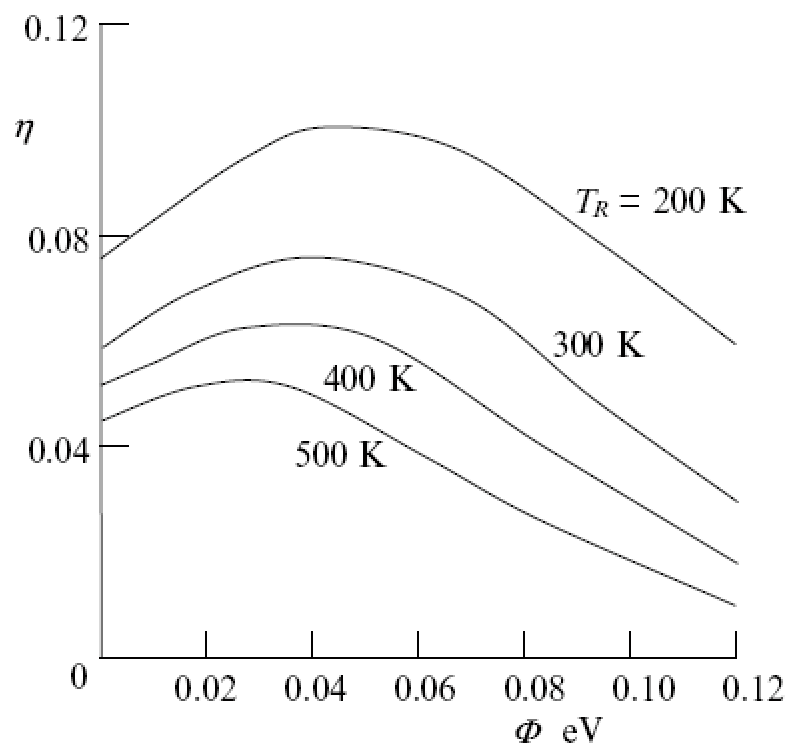


UCSC (Shakouri, Bian, Kobayashi), **Berkeley** (Majumdar), **BSST Inc.** (Bell), **Delaware** (Zide), **Harvard** (Narayanamurti), **MIT** (Ram), **Purdue** (Sands), **UCSB** (Bowers, Gossard)

ONR (2003-2010), DARPA (2008-2012)

Solid-State Thermionic Energy Conversion …according to recent thermoelectric textbooks

Fig. 13.10 Efficiency of a multi-layer thermionic generator plotted against the barrier height. A schematic plot based on the data of Mahan et al. [9]. The source is at 400 K and the sink at 300 K



$$i_{1,2} = A_0 T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

TI figure-of-merit < TE

$$\beta_{\mathrm{I}} = \frac{m^* k (kT)^2 d}{2\pi^2 \hbar^3 \lambda_{\mathrm{L}}}.$$

- **Introduction to Thermoelectricity, J. Goldsmid, Springer 2009**
- **Thermoelectrics: Basic Principles and New Materials Developments. Nolas, Sharp & Goldsmid, Springer-Verlag, 2001**
- **Thermoelectric Handbook: Macro to Nano, ed. D. M. Rowe, CRC 2006**

Modified Richardson equation is not accurate to describe electron transport in superlattices when Fermi energy is few $K_B T$ from barrier height!

Modified Boltzmann transport for Superlattices

$$\sigma = \int \sigma_d(E)dE \qquad S = \frac{1}{eT}\frac{\int \sigma_d(E)(E-E_F)dE}{\int \sigma_d(E)dE} \propto \langle E - E_f \rangle$$

$$K = \frac{1}{eT^2}\left[\int \sigma_d(E)\left[E(\mathbf{k}) - E_F\right]^2 dE - \frac{\left\{\int \sigma_d(E)\left[E(\mathbf{k}) - E_F\right]dE\right\}^2}{\int \sigma_d(E)dE}\right]$$

Differential Conductivity (Transport Function)

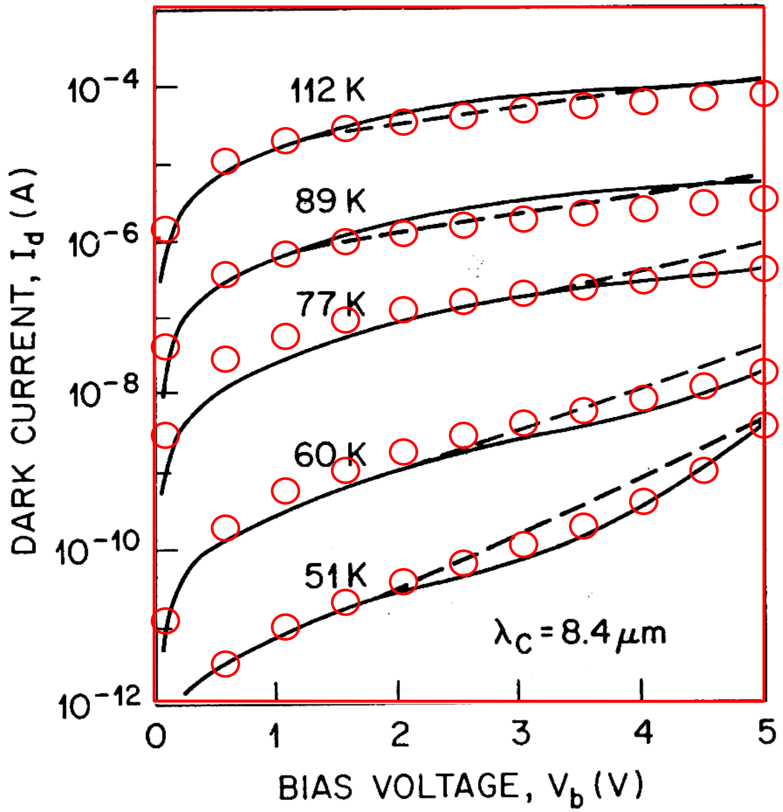
$$\sigma_d(E) = e^2\tau(E)v_x^{\,2}(E)\rho(E)\left(-\frac{\partial f_0(E)}{\partial E}\right)T(E)$$

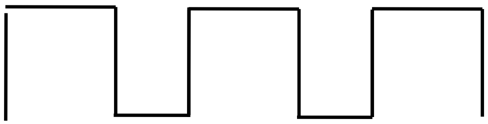
- $T(E)$ → Energy filtering: Tunneling and band edge discontinuity
- $-\frac{\partial f_0(E)}{\partial E}$ → Fermi window: optimal doping
- $\rho(E)$ → Density of states (well/barrier), SL States
- $v_x^{\,2}(E)$ → Group velocity
- $\tau(E)$ → E-dependent scattering, Nanoparticle filtering

Daryoosh Vashaee and Ali Shakouri, Physical Review Letters 2004; JAP 2004
Zhixi Bian and Ali Shakouri, PRB 2007
J-H Bahk, Zhixi Bian and Mona Zebarjadi, 2008

Fitting: Modified Boltzmann transport equation

B.F. Levine, et al., Appl. Phys. Lett. 56(9), 1990





50x GaAs/AlGaAs

(4nm /30.5nm)

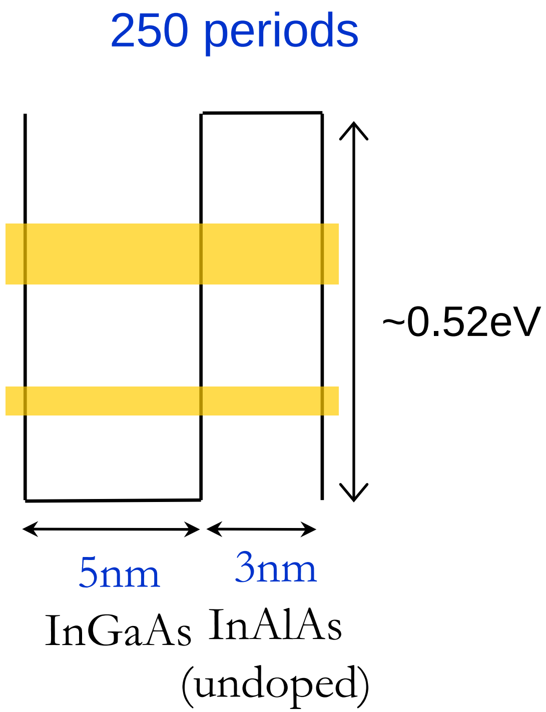
$E_{barrier}$=247meV

$N_{dopant,\ well}$=4x10^{11}cm^{-2}

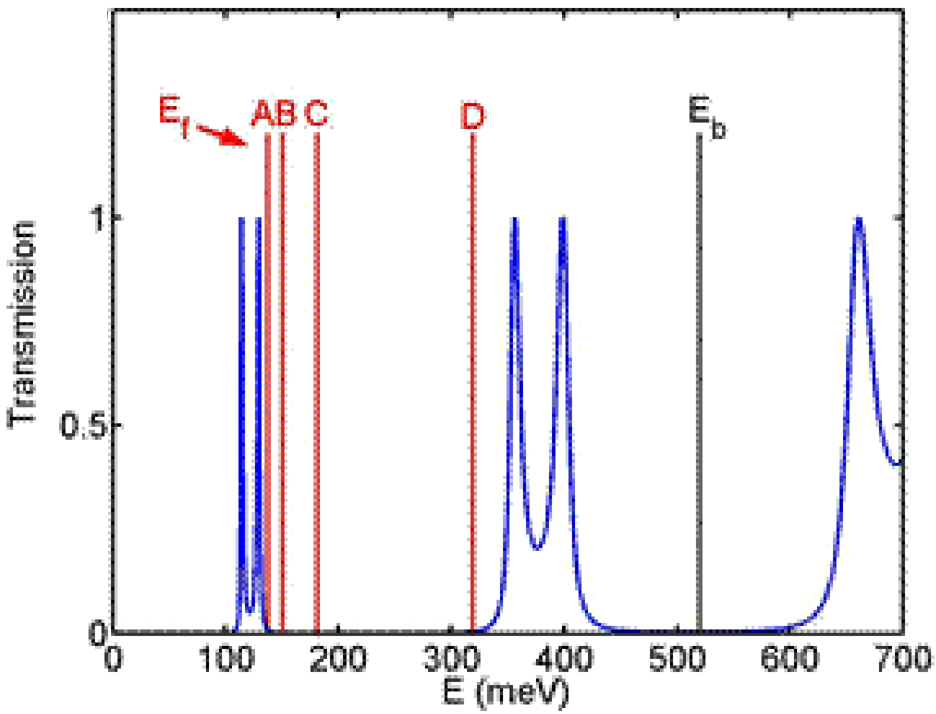
Assumed conserved lateral momentum

D. Vashaee., A. Shakouri, Journal of Applied Physics, Feb. 2004
(InGaAs/InGaAsP superlattices, R. Singh et al. MRS Dec. `03)

TE Properties of short period InGaAs/InAlAs Superlattices



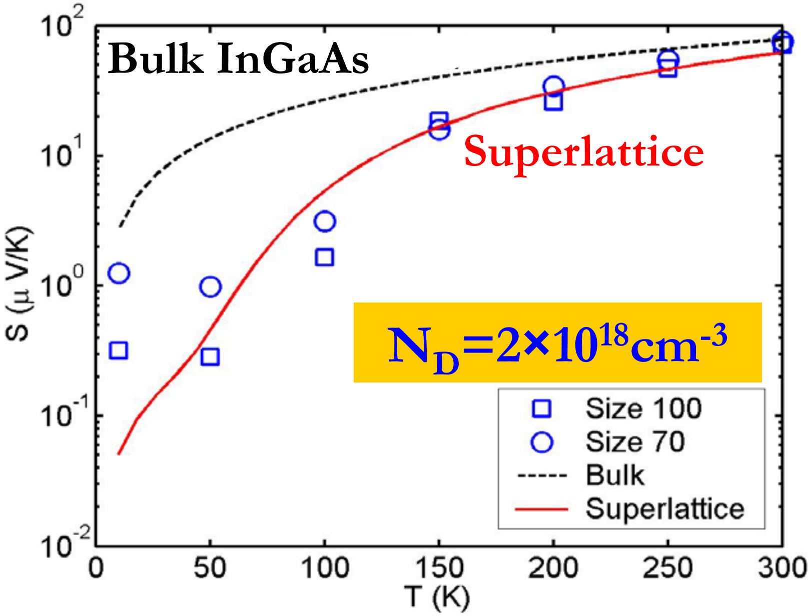
Quantum Mechanical Transmission

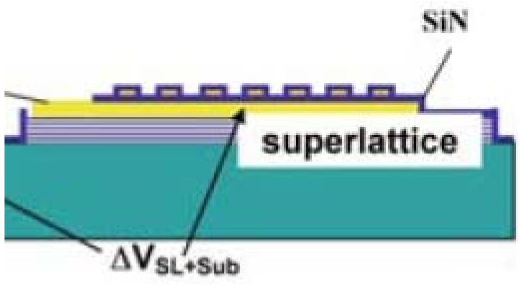


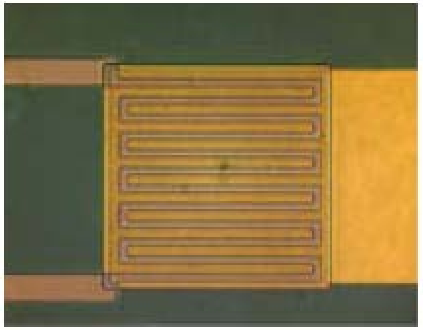
- Tall barriers, short period, miniband transport
- 4 devices with different dopings 2e18 – 3e19cm^{-3}

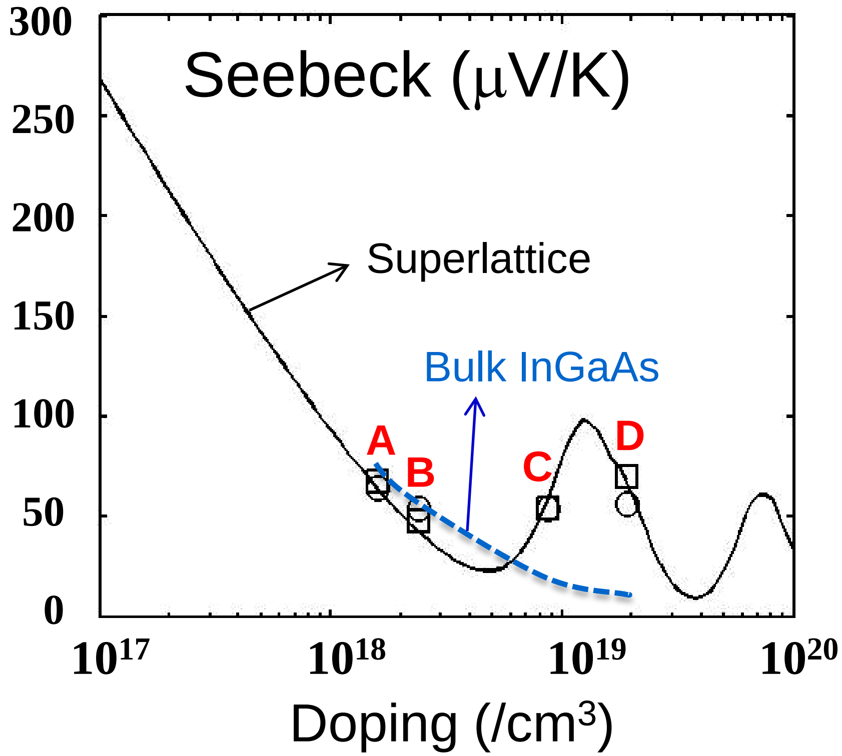
Y. Zhang et al. MRS Fall 2003 Meeting, ICT `04

Cross-plane Seebeck Coefficient (10-300K) Theory vs. Experiment



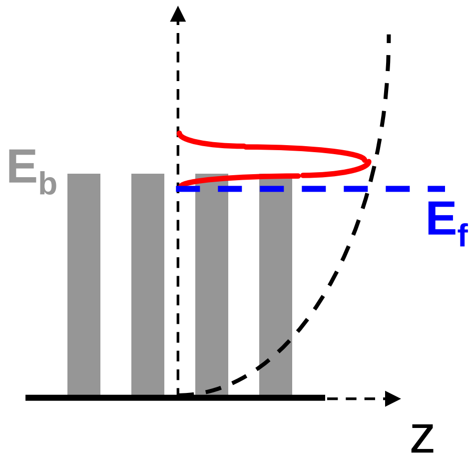


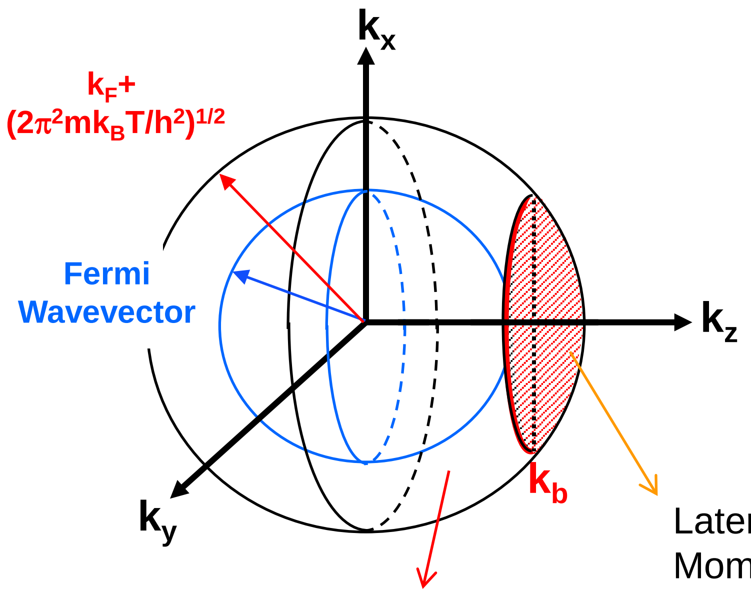




Y. Zhang et al., ICT 2004
D Vashaee, et al, Phys. Rev. B 74, 195315 (2006)

Hot Electron Filtering (Thermionic Emission) in Metallic Superlattices





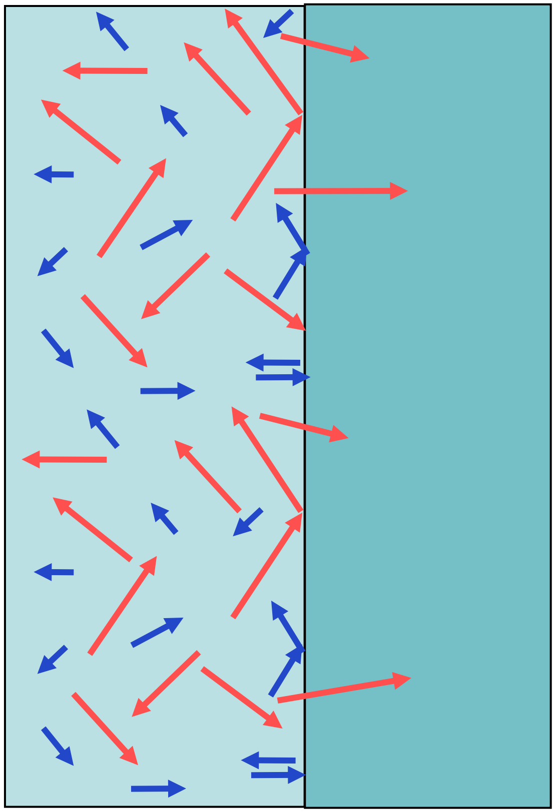
Metallic Superlattice with Tall Barriers

Momentum Space Picture

Planar barrier do not transmit most of the hot electrons if lateral momentum is conserved (momentum filter and not energy filter).

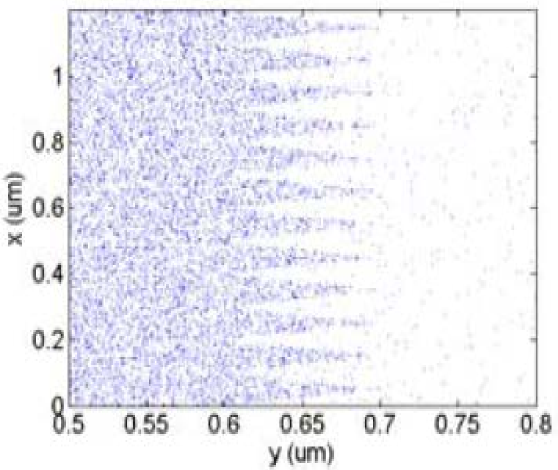
D. Vashaee., A. Shakouri, Physical Review Letters March 12, 2004

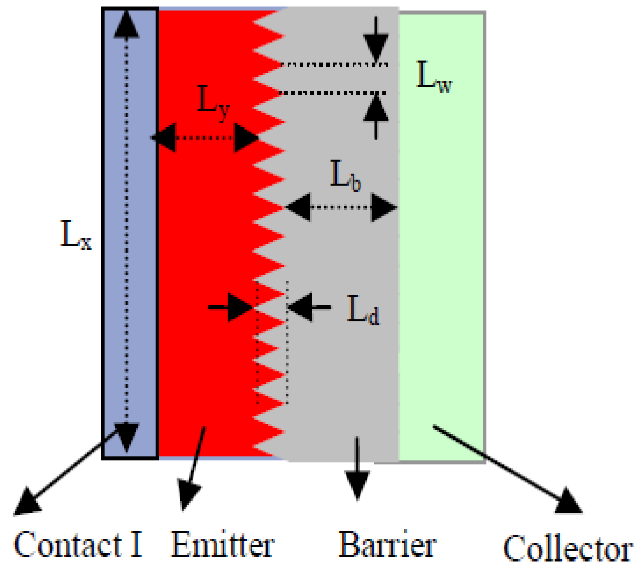
Problem with planar metallic superlattices

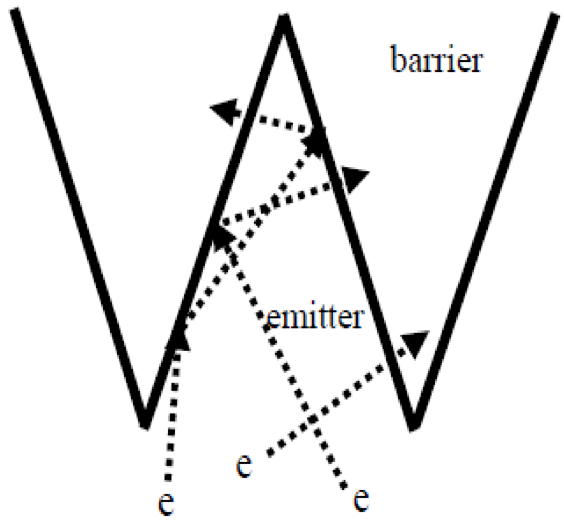


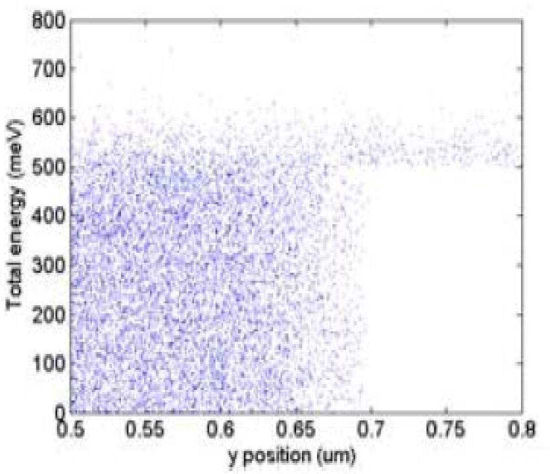
Hot carriers with small kinetic energy in the direction perpendicular to barrier are totally internally reflected.

Nonplanar Barrier for Enhanced Emission





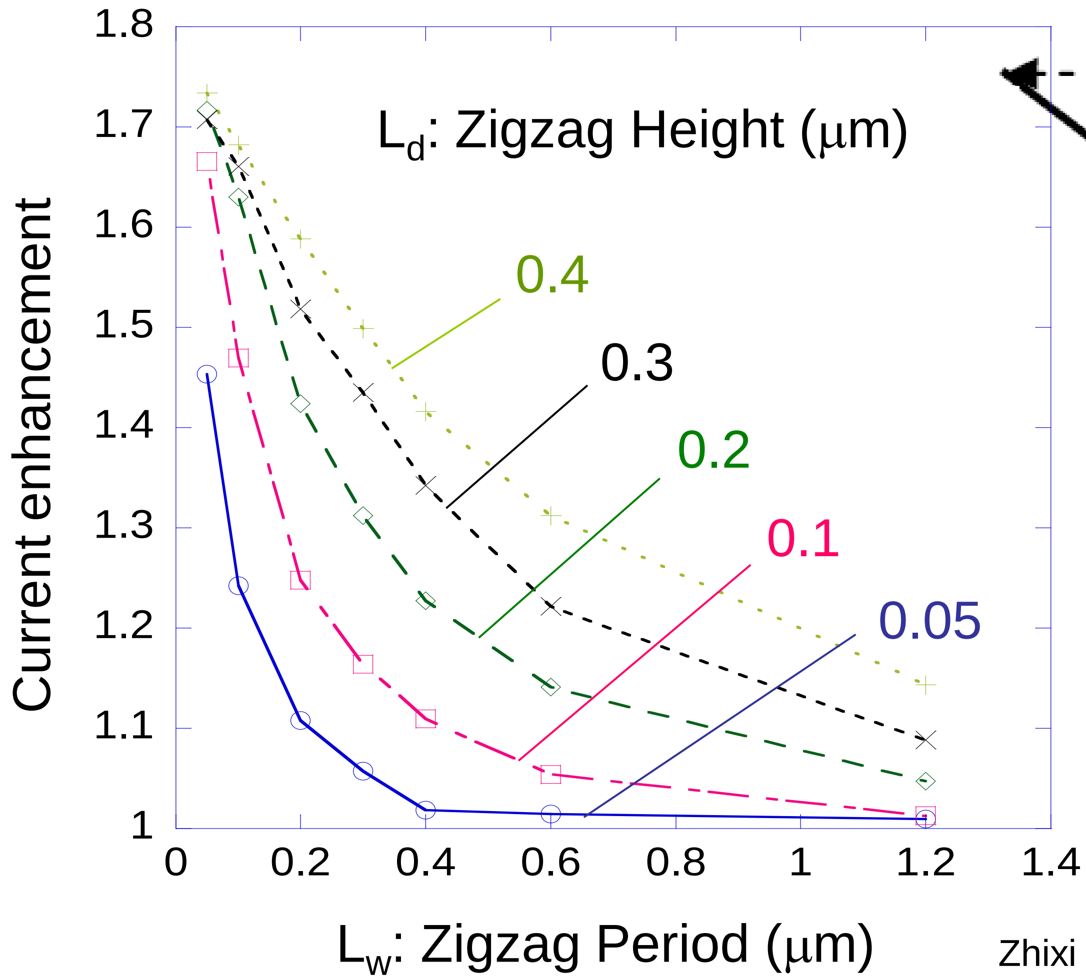


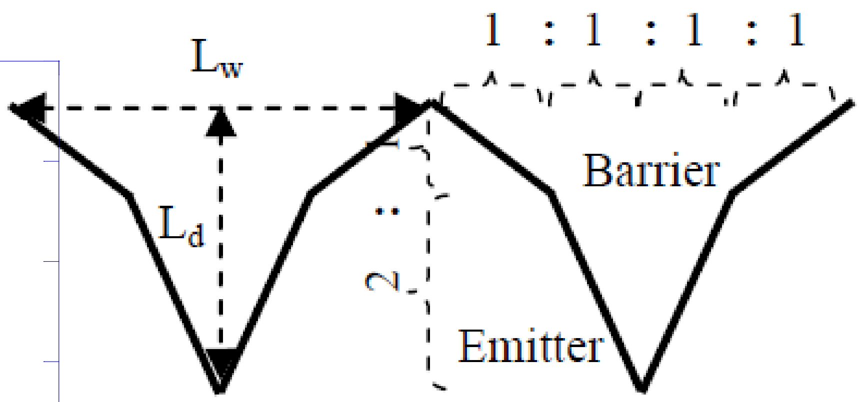


✓Monte Carlo method to simulate nonequilibrium electron transport through complicated heterointerfaces

Zhixi Bian, and Ali Shakouri, "Enhanced solid-state thermionic emission in non-planar heterostructures," *Appl. Phys. Lett*. **88**, 012102 (2006).

Nonplanar Barrier for Enhanced Emission





✓Simulations show the thermionic/thermoelectric transport is enhanced with nonplanar potential barriers

Zhixi Bian, and Ali Shakouri, "Enhanced solid-state thermionic emission in non-planar heterostructures," *Appl. Phys. Lett*. **88**, 012102 (2006).

Week 5: Lecture 1 Summary

- Vacumm thermionic vs. solid-state thermionics
- Modeling of electron transport using Boltzmann Transport Equation (→ Landauer approach)
- Seebeck effect in superlattices (miniband conduction regime vs. thermionic emission)
- Lateral momentum conservation