Thermoelectricity: From Atoms to Systems

Week 5: Recent Advances in Thermoelectric Materials and Physics
Lecture 5.1: Thermionics vs. Thermoelectrics

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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)**

**Energy**

- **Hot electron**
- **Cold electron**

**Cathode**
- Material 1

**Barrier**
- Material 2
- Single Barrier

**Anode**
- Material 1

**Thermionic**: If barrier is thin (< electron energy relaxation length) →

Can not define barrier Seebeck coeff. independent of contact layers
(ballistic, non-linear transport)

**Superlattice**: In linear transport regime can define an “effective”
Seebeck coeff. for the superlattice (linearized TI=TE)
Solid-State Thermionics vs. Thermoelectrics

• 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. Thermoelectrics

- Solid-State Thermionic
  - Interface effect
  - Single barrier non-linear transport \(\Rightarrow\) High Cooling Power Density (Shakouri & Bowers ’97; Shakouri, Lee, Smith, Narayanamurti & Bowers ‘98)
  - Multiple barrier ballistic transport \(\Rightarrow\) High Efficiency (\(\beta\downarrow\)) (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
Symmetry of DOS near Fermi energy is the main factor determining Seebeck coefficient.

A. Shakouri, “Thermoelectric, thermionic and thermophotovoltaic energy conversion”, ICT 2005
Even with only modestly low lattice thermal conductivity and electron mobility of typical metals, $ZT > 5$ is possible with hot electron filters.

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

$\text{ONR (2003-2010), DARPA (2008-2012)}$
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

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

\[ \beta_I = \frac{m^* k (kT)^2 d}{2\pi^2 \hbar^3 \lambda_L} \]

TI figure-of-merit < TE

- Introduction to Thermoelectricity, J. Goldsmid, Springer 2009

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

\[ \sigma = \int \sigma_d(E) dE \]

\[ S = \frac{1}{eT} \int \frac{\sigma_d(E)(E - E_F) dE}{\sigma_d(E) dE} \propto <E - E_f> \]

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

**Differential Conductivity (Transport Function)**

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

- Energy filtering: Tunneling and band edge discontinuity
- Fermi window: optimal doping
- Density of states (well/barrier), SL States
- Group velocity

**E-dependent scattering**

Nanoparticle filtering

**References**

Zhixi Bian and Ali Shakouri, PRB 2007
Low Temp. I-V in GaAs/AlGaAs Superlattices

Fitting: Modified Boltzmann transport equation

(InGaAs/InGaAsP superlattices, R. Singh et al. MRS Dec. `03)


50x GaAs/AlGaAs
(4nm /30.5nm)
E_{\text{barrier}}=247\text{meV}
N_{\text{dopant, well}}=4\times10^{11}\text{cm}^{-2}

Assumed conserved lateral momentum
TE Properties of short period InGaAs/InAlAs Superlattices

- Tall barriers, short period, miniband transport
- 4 devices with different dopings $2 \times 10^{18} - 3 \times 10^{19} \text{cm}^{-3}$

Y. Zhang et al. MRS Fall 2003 Meeting, ICT ’04
Cross-plane Seebeck Coefficient (10-300K) Theory vs. Experiment

\[ N_D = 2 \times 10^{18} \text{cm}^{-3} \]

Y. Zhang et al., ICT 2004
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 and cold electrons in equilibrium
- Hot electron filter

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

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