Nanostructured semiconductors for thermoelectric applications: a theoretical perspective

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Thermoelectrics

- Convert **heat** flow directly to **electricity** (no moving parts!)
- Thermoelectric **figure of merit**
  - $\sigma$ electrical conductivity
  - $S$ thermopower (Seebeck coeff.)
  - $\kappa$ thermal conductivity
- **Nanostructuring** primarily allows us to reduce $\kappa_{\text{ph}}$ due to scattering of the phonons at interfaces
- Sometimes nanostructuring may be beneficial for the electrical properties, too.

$$ZT = \frac{\sigma S^2}{\kappa_{\text{el}} + \kappa_{\text{ph}}} T$$
Materials

semiconductors with (mostly) small band gap, or semimetals

suitability depends on operation temperature range

This talk
Applications

- Thermoelectric generator for space mission
- Radioisotope as energy source
- High-temperature application

SiGe thermocouple
Applications

- waste heat recovery in cars
- additional electricity for on-board electronics
Thermoelectric muffler

- Medium-range application
- Various materials in use: PbTe, skutterudites, half-Heusler alloys
Thermal conductivity of SiGe heterostructures: Can we beat the “alloy limit”?
**Impact of Ge surface segregation-driven intermixing on $\kappa$**

**Sample structure:** Ge/Si superlattices, fixed Si thickness, variable Ge thickness

<table>
<thead>
<tr>
<th>Ge layer n monolayer</th>
<th>Si spacer: 6 nm</th>
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<tbody>
<tr>
<td>Ge layer n monolayer</td>
<td>Si buffer 80 nm</td>
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| Si (001) Substrate |

**Measurements:** thermal conductivity from $3\omega$ method at $T = 300$ K

**Results:**

Ge segregation leads to cross-plane thermal conductivity $\kappa$ lower than for superlattices with sharp interfaces, or for the equivalent alloys.

Impact of Ge surface segregation-driven intermixing on $\kappa$

**Phonon filtering by reduction of the mean free path:**

**Sharp interfaces:**
- low frequency phonons $< 3$ THz

**Alloys:**
- high frequency phonons $> 3$ THz

**Realistic interfaces:** combined advantages of the two extremes.

Band structure engineering: Ge quantum dot crystals in Si host

image from:
Can we further improve on electrical properties?

- Boltzmann approach to transport
  
  $\sigma = e^2 L^{(0)}; \quad S = -\frac{e}{T} \frac{L^{(1)}}{L^{(0)}}; \quad \kappa_{el} = \frac{L^{(2)}}{T} - \frac{e}{T} \left( \frac{L^{(1)}}{L^{(0)}} \right)^2$

\[ L^{(\gamma)} = \int d\varepsilon \sum_n \left( -\frac{\partial f^{(0)}}{\partial \varepsilon} \right) g_n(\varepsilon) \tau_n(\varepsilon) v_n^2 (\varepsilon - \mu)^\gamma \]

- tight-binding calculation using relaxed positions: sp$^3$ Hamiltonian with distance-dependent 1$^{\text{st}}$ & 2$^{\text{nd}}$ neighbour matrix elements, spin-orbit splitting
- Density of states $g_n$ and velocities $v_n$ follow directly from electronic structure
- Remaining challenge: calculation of relaxation time $\tau_n(\varepsilon)$

Can we further improve on electrical properties?
Atomistic theory for nanostructures

- periodically repeated supercell with 6 $\text{Si}_{0.5}\text{Ge}_{0.5}$ layers & pure Ge quantum dot 8 layers high
- atomic positions are relaxed using a Tersoff force field
- tight-binding calculation using relaxed positions: $\text{sp}^3$ Hamiltonian with distance-dependent 1$^{\text{st}}$ & 2$^{\text{nd}}$ neighbour matrix elements, spin-orbit splitting
- iterative eigenfunction solver for selected electronic states

![Graph showing biaxial strain $\varepsilon_{xx} - \varepsilon_{zz}$ in yz-plane](image)
electronic states in nanodot crystal

derived from valleys in $k_x$ or $k_y$

$|\text{wavefunction}|^2$

→ system can be modeled by a 2D electron gas laterally confined between the nanodots
Scattering rate in 2D or 3D systems

- **Mechanisms included**: impurity scattering, acoustic phonon scattering, intervalley phonon scattering
- **Deformation potentials** empirically known (from Si MOS 2DEG); e.g.

\[
\frac{1}{\tau_{nm}(\varepsilon)} = \frac{D_0^2m_T}{\hbar^2 \rho_m \omega_0} |I_{nm}|^2 \left( n(\omega_0)\Theta(\varepsilon - \varepsilon_m + \hbar \omega_0) + (n(\omega_0) + 1)\Theta(\varepsilon - \varepsilon_m - \hbar \omega_0) \right)
\]

- **Matrix elements** calculated specifically from the tight-binding wavefunctions

<table>
<thead>
<tr>
<th></th>
<th>( I_{00} )</th>
<th>( I_{01} )</th>
<th>( I_{11} )</th>
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<tbody>
<tr>
<td>g-process</td>
<td>17.39</td>
<td>12.65</td>
<td>18.75</td>
</tr>
<tr>
<td>f-process</td>
<td>2.61</td>
<td>6.45</td>
<td>11.70</td>
</tr>
</tbody>
</table>

Scattering rate at \( n_D = 10^{17} \text{ cm}^{-3} \) and \( T = 100 \text{K} \) for

- lowest subband
- 2nd lowest subband
Quantum dot array: Properties

- High mobility → high conductivity due to perfectly crystalline heterostructures
- “Early rise” of ZT; higher values achievable than with SiGe alloys

![Graphs showing doping levels and thermal conductivity](image)

Half-Heusler alloys: a new class of ternary semiconductors

The STEM image shown in Fig. 1(a) implies as smooth boundaries between layers. Additionally, the selected area electron diffraction (SAED) pattern provides evidence for the presence of TiNiSn. The high-resolution STEM image (Fig. 1(c)) clearly reveals the presence of TiNiSn in the cross-section of the SL. Observed diffraction spots confirm the orientation of the film reflections. The inset in Fig. 1(a) shows a high-resolution STEM image of a circular region marked in Fig. 1(a). Based on these observations, it can be concluded that not only the positions of the peaks but also the overall peak shapes agree well. However, relative intensities of the peaks are not exactly reproduced, especially for higher-order satellites, indicating disturbances from the substrate. Due to the slight difference between the lattice constants of both HH materials, we also observe a splitting of the reflection indicated by an arrow. Unequal lattice constants lead to the distortion of the lattice visible in the high-resolution STEM image. The STEM dark field image of a SL cross section with a period of 4 nm, composed of TiNiSn (dark contrast) and HfNiSn (bright contrast) and surface topography of an approximately 800-nm-thick SL with rms roughness of 1.1 nm (AFM image) in the inset. (b) SAED of a circular region from the image in panel (a). (c) High-resolution STEM image. (d) The magnification of a rectangular region with the assignment of atoms.
Why half-Heusler alloys?

Ternary alloys from an early transition metal, a late transition metal, and a group-IV or V element allow for many combinations with a wide range properties.

➔ “engineered” heterostructures

www.uni-due.de/physik/kratzer
Requirements for heterostructures

Thermal conductivity is reduced by interfaces …

• growth of thin layers (tens of nanometers)
• good lattice match between the materials
• but: widely different phonon modes / mass densities

…while the advantageous electrical properties are retained.
• Combination of narrow and wide gap semiconductors,
  but with
• one band (valence or conduction band) closely matched

Strategy:
keep one chemical component, vary the other two, so as to fulfill the electron count for semiconducting half-Heusler alloy.
Bulk materials with group IVb

Family of small-gap semiconductors

ZrNiSn

TiNiSn

HfNiSn

0.42 eV

0.46 eV

0.34 eV

3% mismatch
Bulk materials with group IVb

Wide-gap insertion

Ni → Co
Sn → Bi

→ Barrier in the conduction band

ZrNiSn

0.46 eV

1.5% mismatch

ZrCoBi

1.01 eV
Phonon band structures

- calculated from first principles using density functional perturbation theory*
- shown in (110) direction
- six low-lying optical modes

* S. Baroni et al., Rev. Mod. Phys. 73, 515 (2001)
Diffuse Mismatch Model

- **bulk conductivity**
  \[
  \kappa_{A, \text{bulk}} = \frac{1}{8\pi^2} \sum_{j} \int_{q_j} \hbar \omega(q_j) |v(q_j)| \ell_{A}(q_j) \frac{df_0}{dT} q_j^2 dq_j
  \]
  with mean free path
  \[
  \ell_{A}(q_j) = \frac{C |v_{A}(q_j)|}{\omega_{A}^2(q_j) T}
  \]
  with known numerical constant \( C = 10^{18} \text{ K/s} \)

- Transmission probability \( \xi_{A \rightarrow B} \)
determined* by phonon density of states

\[
\xi_{A \rightarrow B}(\omega) = \frac{\sum_{j} q_{j,B}^2(\omega)}{\sum_{j} q_{j,A}^2(\omega) + \sum_{j} q_{j,B}^2(\omega)}
\]

Superlattice thermal conductivity

• Matthiessen’s rule for interface plus bulk scattering

\[
\frac{1}{\ell_A(q)} = \frac{1}{d_A \xi_{A \rightarrow B}(\omega_A(q))} + \frac{\omega^2_A(q)T}{C|v_A(q)|}
\]

with known numerical constant \( C = 10^{18} \, \text{K/s} \)

\[ d_A = d_B = 20\text{nm} \]

• Factor 3 reduction of thermal conductivity even at 600K !

Experimental test

- TiNiSn/HfNiSn superlattices of varying period $d_A + d_B$, but fixed overall sample thickness

![Graph showing $\kappa$ vs. superlattice period length [nm]]

Experimental data (room temp.)

... and how about the electrical properties?

- Band offset and quantum confinement in superlattices

- Perform *ab initio* band structure calculations (density functional theory) for ultra-short period superlattices!

(110) interface 1+1 bi-layers
Ultra-thin layers

thermoelectric data evaluated at T=600K

\[ S \text{[\(\mu V/K\)]} \]

... assuming \( \tau = 10^{-14} \text{s} \)

Density of states

\begin{align*}
\text{CB} & \quad \text{1+1 bilayer} \\
& \quad \text{2+2 bilayers} \\
& \quad \text{1+3 bilayers}
\end{align*}

\[ \text{VB} \]

Overall performance estimates

- **Thermal conductivity** $\kappa$ from ideally crystalline bulk + interface resistivity obtained from Diffuse Mismatch Model
- **Doping** is assumed to bring the Fermi level to the VB or CB edge of the structure under investigation
- Electronic *relaxation time* assumed $\tau = 10^{-14}$ s
- Theoretical estimate for *figure-of-merit* $ZT$ at $T = 600$K

<table>
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<tr>
<th></th>
<th>pure ZrNiSn</th>
<th>+ ZrCoBi barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-type</td>
<td>0.20</td>
<td>0.38</td>
</tr>
<tr>
<td>n-type</td>
<td>0.13</td>
<td>0.44</td>
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- For n-type, **factor 3 improvement** carries over from $\kappa$ to $ZT$ !
Summary

• **Interface resistivity** reduces the thermal conductivity of a heterostructure stack; it is estimated on the basis of harmonic phonon modes.

• In Ge/Si quantum dot crystals, **strain-induced conductive channels** allow for higher electrical conductivity, and thus higher thermoelectric power.

• **ZT value** starts to rise already above room temperature and reaches ZT=2.0 at T=1000 K

• In the ternary **half-Heusler compounds**, the freedom of chemical composition allows for engineering both the **electronic** and the **phononic band structure**.

• A **superlattice** of two half-Heusler materials allows to reduce the thermal conductivity and thus to **improve ZT**.
Acknowledgments

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Thank you for your attention!