Quantum Dot Superlattices as Perspective Materials for Thermoelectric Applications

O.L. Lazarenkova, A.A. Balandin
Y. Bao, and J.L. Liu
Department of Electrical Engineering
University of California - Riverside
Summary

Under certain conditions quantum dots (QDs) may form highly regimented three-dimensional (3D) quantum dot arrays characterized by unique carrier and phonon spectra. We refer to such novel nanostructured materials as quantum dot crystals (QDC). By changing the size of QDs, inter-dot distance and dot regimentation one can tune both electron [1] and phonon [2] spectra of QDC. In this presentation we demonstrate that thermoelectric properties of such structures can also be significantly enhanced [3]. The thermoelectric figure of merit improves when electrical conductivity and thermoelectric power increase while thermal conductivity decreases. The interaction between regimented quantum dots leads to splitting of discrete electron energy levels of single QD and formation of the mini-bands. It results in nonlinear electrical conductivity and electron part of thermal conductivity as well as sign switching of the thermoelectric power. On the other hand, the existence of 3D periodic scatters, e.g. QDs, leads to folding of acoustical phonon modes, formation of mini-gaps, and emergence of the low-energy quasi-optical modes. This results in reduction of the phonon part of thermal conductivity. These factors lead to the enhancement of thermoelectric figure of merit. Together with an additional benefit of using the same type of QDC for both legs of thermoelectric device it makes QDC very attractive as perspective materials for thermoelectric applications.

Regimented Quantum Dot Arrays and 3D Superlattices

- Reported 3D regimented quantum dot superlattices: pyramidal PbSe dots on PbTe (111) with {100} side facets. After G. Springholtz, et al., Science, Vol. 282, p.734-737

**From regimented quantum dot superlattices (QDS) to quantum dot crystals (QDC)?**
Increase the Thermoelectric Figure of Merit in QDS

- **ZT enhancement in quantum wells and quantum wires related to confinement of carriers**
  - change in the electronic density of states near $E_F$
  - semimetal – semiconductor transitions due to confinement
- 2D is better than bulk, 1D is better than 2D
- Is quasi-0D is better than 1D?
  - *Hopping or above-the-barrier carrier conduction is no good*…
  - *One needs mini-bands to form*
- **ZT increase due to decrease in the lattice thermal conductivity**
  - Increased phonon - rough interface scattering when thickness $W \leq$ phonon MFP
  - Decreased in-plane phonon group velocity due phonon confinement effect (spectrum modification) in 2D and 1D structures when $\Lambda \sim W \ll$ MFP

**Figure of merit:**

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$
Modeling of Electron and Phonon Dispersion in QDS

Prototype structure and assumptions

**Conditions for phonon spectrum modification:**
- Nanostructure feature size \( W \) is smaller than dominant phonon mean free path (MFP)
- \( W \) comparable to thermal phonon wavelength
- Acoustic mismatch between constituent materials

**Conditions for carrier mini-band formation:**
- Quantum dots are regimented and the dot size is homogeneous
- Inter-dot distance and barrier height are small for strong function overlap
- Dots are crystalline with low interface defects
Heavy-hole dispersion in Ge/Si QDS along [[111]] quasi-crystallographic direction.

Parameters:
Lx=Ly=5 nm; Lz=2.5 nm; Hx=Hy=2.5 nm; Hz=1.25 nm

Potential well depth: V=450 meV

Energy is counted from the position of the barrier.
Electrical Conductivity of Quantum Dot Superlattices

Conductivity (S/m)

$E_{111}$

InAs/GaAs

$\sigma_{zz}$

$\sigma_{xx} = \sigma_{yy}$

$T = 300 \text{ K}$

Electric conductivity at room temperature of simple cubical $p$-doped Ge/Si QDS
Calculation of Thermoelectric Characteristics

Figure of merit: \( ZT = \frac{\alpha^2 \sigma T}{\kappa} \)

Boltzmann equation is solved in RTA:

\[
\begin{align*}
\sigma &= S_0 \\
\alpha &= -\frac{1}{eT} S_0^{-1} S_1 \\
\kappa_e &= \frac{1}{e^2 T} \left(S_2 - S_1 S_0^{-1} S_1\right)
\end{align*}
\]

\[
S_\xi = e^2 \int \frac{4dq}{\pi^2 d^2} \left( -\frac{df}{d\epsilon} \right) \tau(q) \nu(q) \nu(q)[\epsilon(q) - E_F]^\xi
\]

\[
S_{\xi,ij} = \frac{e^2}{4\pi^2 k_B T h^2} \int d\epsilon dq \left[ \tau(\epsilon(q)) (\epsilon(q) - E_F)^\xi \right] \frac{\exp[(\epsilon(q) - E_F)/k_B T]}{\{\exp[(\epsilon(q) - E_F)/k_B T] + 1\}^2} \frac{\partial \epsilon(q)}{\partial q_i} \frac{\partial \epsilon(q)}{\partial q_j}
\]

**Step I:** use exact carrier dispersion, combined relaxation time \( \tau \), some \( K_{ph} \)

**Step II:** use carrier and phonon dispersion, calculated electron – phonon scattering, some \( K_{ph} \)

**Step III:** in addition to Step II, calculate \( K_{ph} \) taking into account phonon spectrum modification.
Seebeck Coefficient of Ge/Si QDS

Fermi Energy (eV)

Seebeck coefficient of simple cubical Ge/Si QDS

Parameters:

\( L = 2.5 \, \text{nm} \),
\( H = 1.0 \, \text{nm} \),
\( V_e = 0.45 \, \text{eV} \),
\( m^*_{W} = 0.28 \, m_0 \),
\( m^*_{B} = 0.49 \, m_0 \),
\( T = 300 \, \text{K} \),
Calculation of the Acoustic Phonon Dispersion in QDS

For $x$-component of the displacement vector

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \frac{\partial}{\partial x} c_{11} \frac{\partial u_x}{\partial x} + \frac{\partial}{\partial y} c_{44} \frac{\partial u_x}{\partial y} + \frac{\partial}{\partial z} c_{44} \frac{\partial u_x}{\partial z}$$

$$+ \frac{\partial}{\partial x} c_{12} \frac{\partial u_y}{\partial y} + \frac{\partial}{\partial x} c_{12} \frac{\partial u_z}{\partial z} + \frac{\partial}{\partial y} c_{44} \frac{\partial u_y}{\partial x} + \frac{\partial}{\partial z} c_{44} \frac{\partial u_z}{\partial x}$$

For $y$-component replace $x \rightarrow y, y \rightarrow z, z \rightarrow x$.

For $z$-component replace $x \rightarrow z, y \rightarrow x, z \rightarrow y$.

In subscripts of elastic constants

1 $\equiv xx$ - strain along the displacement
2 $\equiv yy$ - strain perpendicular to the displacement
4 $\equiv yz$ - tangential strain

There are 15 nonzero components in every $3(\mathcal{N}_x\mathcal{N}_y\mathcal{N}_z)$ row

Eigenvalues $\lambda_i = \omega_i^2$
Both quasi-acoustical and quasi-optical vibrations exist at low energy.

Quasi-optical waves oscillating inside or between quantum dots are almost localized.

Phonon carrier scattering increases.

$L_x = L_y = 5.0 \text{ nm}$,
$H_x = H_y = 2.5 \text{ nm}$,
$H_z = 1.25 \text{ nm}$.
Comparison of Phonon Dispersion in PbSeTe/PbTe and Ge/Si QDS

PbSe$_{0.98}$Te$_{0.02}$/PbTe QDC
$L_x=L_y=15\text{nm}, L_z=5\text{nm}$
$D_x=D_y=30\text{nm}, D_z=10\text{nm}$

Ge/Si QDC
$L_x=L_y=15\text{nm}, L_z=5\text{nm}$
$D_x=D_y=30\text{nm}, D_z=10\text{nm}$
Normalized ZT of QDS

**Figure:** Room temperature Seebeck coefficient for QDS normalized to the bulk Si value vs Fermi energy. Note an order of magnitude ZT increase in a wide range of QDS parameters over bulk Si value. The inset shows ZT for the bulk Si vs Fermi energy. The structure is characterized by the following parameters: $L = 2.5$ nm, $H = 1.0$ nm, $V_e = 0.45$ eV, $m^*_{W} = 0.28 \ m_0$, and $m^*_{B} = 0.49 \ m_0$. 

**Graph:**
- **$ZT_{QDS}/ZT_B$** vs Heavy Hole quasi-Fermi Energy (eV)
- **$ZT_B$** vs $E_F$ (eV)

Legend:
- **QDS with bulk lattice thermal conductivity of 156 W m$^{-1}$K$^{-1}$**
- **QDS with reduced lattice thermal conductivity of 15 W m$^{-1}$K$^{-1}$**
Si/Ge Quantum Dot Superlattices

- Density of Ge quantum dots extracted from SEM: $3 \times 10^9$ cm$^{-2}$
- Typical dot parameters as grown: base: 70 nm; height 15 nm

SEM micrograph of MBE grown Ge/Si QDS.
## Preliminary Experimental Results

### Measurement of Hall mobility of Ge/Si QDS

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<th>Sample</th>
<th>Period</th>
<th>Sign of Hall voltage</th>
<th>( \mu \text{ 300K cm}^2/\text{VS} )</th>
<th>( \rho \text{ 300K Ohm cm} )</th>
<th>( \text{Ns 300K cm}^{-2} )</th>
<th>( \mu \text{ 77K cm}^2/\text{VS} )</th>
<th>( \rho \text{ 77K Ohm cm} )</th>
<th>( \text{Ns 77K cm}^{-2} )</th>
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Related Publications and Acknowledgement


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