Carrier and Phonon Spectrum in Quantum Dot Superlattices for Optoelectronic and Thermoelectric Applications

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ABSTRACT
Quantum dot superlattices, e.g. multiple arrays of quantum dots, have been recently proposed for optoelectronic and thermoelectric applications. In this paper we present two models for calculating carrier spectrum in regimented three-dimensional quantum dot superlattices, e.g. artificial quantum dot crystals. The models are based on semi-analytical Kronig-Penny-type and the finite-different numerical solutions of the Schrödinger equation. The phonon spectrum in quantum dot superlattice is found from the numerical solution of the elasticity equation with piece-wise uniform parameters of constituent materials. It is demonstrated that carrier and phonon spectra in such structures undergo significant modification and differ from those in bulk materials and conventional quantum well superlattices. The proposed models can be used for structure optimization tailored to specific applications.

Keywords: quantum dot superlattice, quantum dot crystal, confined phonons, nanostructures, thermoelectrics.

1. THEORETICAL MODEL
We consider three-dimensionally (3D) regimented QDS with the strong coupling (wave function overlap) among the dots. QDS with 3D regimentation has been reported in literature [1]. Strong coupling and regimentation leads to formation of 3D extended mini-bands instead of localized quantum dot states. This makes such structures analogous to artificial crystals, e.g. quantum dot crystals [2]. Such energy spectrum modification is expected to take place provided that the dot size is homogeneous and the dots are crystalline with low surface defect concentration. Formation of extended electron states and mini-bands have also already been observed in multiple quantum-dot arrays [3-4].

We calculate electron spectrum of QDS in the envelope wave function approximation applied to a potential barrier profile of choice. The one-electron Schrödinger equation for such a system is written as

\[
\frac{-\hbar^2}{2m} \nabla_r \cdot \frac{1}{m} \nabla_r + V(r) \phi(r) = E \phi(r)
\]  

where \( \hbar \) is Plank’s constant, \( 1/m^* \) is the reciprocal effective mass tensor, \( \phi(r) \) is the electron wave function, \( E \) is the electron energy, and the confining potential profile \( V(r) \) corresponds to an infinite sequence of quantum dots of size \( L_x, L_y, \) and \( L_z \) separated by the barriers of thickness \( H_x, H_y, \) and \( H_z \). The profile \( V(r) \) is set to zero in the barrier region, while inside quantum dot it is equal to the band offset in the conduction (or valence) band of the considered material system taken with a negative sign. The information about band structure of the host materials is reflected in the reciprocal effective mass tensor \( 1/m^* \). The effect of strain was approximately taken into account by changing the value of the corresponding band offset. The confining potential \( V(r) \) was considered to be a piece-wise uniform function.

Heat in semiconductors is mostly carried by acoustic phonons. Acoustic phonon dispersion is strongly modified in QDS. In the long-wavelength limit, the dispersion can be described by a continuum model. For QDS made of semiconductors of cubic symmetry, such as Si and Ge with diamond lattice (\( O_h \) space group), or \( \text{AB}_5 \) compounds with zinc-blende lattice (\( T_d \) space group) the number of independent elastic stiffness constants in the elasticity equation for heterogeneous system reduces down to three:

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial}{\partial x} \left( c_{11} \frac{\partial u_i}{\partial x} + c_{44} \frac{\partial u_i}{\partial y} + c_{44} \frac{\partial u_i}{\partial z} \right) + \frac{\partial}{\partial y} \left( c_{12} \frac{\partial u_i}{\partial y} + c_{44} \frac{\partial u_i}{\partial x} + c_{44} \frac{\partial u_i}{\partial z} \right) + \frac{\partial}{\partial z} \left( c_{12} \frac{\partial u_i}{\partial z} + c_{44} \frac{\partial u_i}{\partial y} + c_{44} \frac{\partial u_i}{\partial x} \right)
\]

(2)

Similar expressions for \( y \)- and \( z \)-components of the displacement vector \( \mathbf{u} \) of a geometrical point inside the material of QDC with \( (i = x, y, z) \) coordinates can be obtained by cyclic exchange of \( (u_x, u_y, u_z) \) and \( (x, y, z) \). The Eq. (2) results from Euler-Lagrange equations for the heterogeneous system with cubical crystal lattice. The solution of these equations for QDS can be expressed in a plane-wave form by analogy with regular bulk crystals

\[
\mathbf{u}(r,t) = \mathbf{A}(r) \exp[i(\mathbf{q} \cdot r - \omega t)]
\]

(3)
where \(|q| = 2\pi/\lambda\) is the phonon wave vector, with phonon wavelength \(\lambda\), \(r\) is coordinate vector, \(t\) is time, and \(\omega\) is the phonon frequency.

We solve Eqs. (1-2) using the finite difference method (FDM) algorithm, details of which were reported elsewhere [5]. A simpler semi-analytical approach to calculate electron dispersion below the potential barrier in QDS with a model confining potential that allows for electron wave function separation has been reported in Ref. [2].

3. RESULTS AND DISCUSSION

As an example material system we consider Ge quantum dots grown on (001) Si by the molecular beam epitaxy (MBE). Although state-of-the-art Ge/Si QDS are characterized only by partial regimentation, continuous progress in MBE self-assembly most likely will lead to synthesis of 3D regimented quantum dot superlattices similar to those reported in Ref. [1]. For simplicity we restrict our analysis to heavy-holes in Ge/Si QDS. This is done for two reasons. Firstly, most of the band-gap discontinuity between Si and Ge goes to the valence band. Secondly, we can use the single-valley effective mass approximation since a single potential energy maximum in the valence band is located in \(\Gamma\) point. In addition, our calculations are facilitated by the fact that the light-hole sub-band in compressed Ge is well separated from the heavy-hole sub-band and have much smaller effective mass, e.g. larger quantum confinement energies. The spin-orbit split-off sub-band in Ge is omitted from consideration since even in relaxed bulk material it is separated from the heavy-hole sub-band with \(E(\Gamma_7) = -290\) meV energy gap and the mini-bands emanating from this sub-band do not contribute significantly to the mostly below-the-barrier mini-band transport.

In order to find the carrier spectrum we solve Schrödinger equation using two different approaches. In the first one, we use a model confining potential that allows for carrier wave function separation and semi-analytical solution [2]. In the second approach, we solve the equation directly using the finite-difference method [3]. We find good agreement of the results for the below-the-barrier states, which validates further use of the simplified semi-analytical model for carrier transport and optical spectrum calculations.

Fig. 1 shows the heavy-hole dispersion in of Ge/Si QDS calculated using FDM. The energy is given with respect to the position of the potential barrier. Double brackets for the wave vector notation are introduced to distinguish direction in quantum dot super crystal from crystallographic directions in the host materials.

One can see the transformation of discrete levels of isolated quantum dots to mini-bands in 3D regimented quantum dot arrays. Similar to bulk crystals, the energy in QDS has the full symmetry of the reciprocal lattice. In this artificial crystal some of the energy bands are degenerate in the center of the quasi-Brillouin zone (QBZ). Moving away from the point of high symmetry in the center of QBZ to a point of lower symmetry splits the energy branches. The width of mini-bands rapidly increases with shrinking of distance between quantum dots and may be up to dozens meV as we have demonstrated in Ref. [2]. The existence of the mini-band means that electron (or hole) state is extended over the whole QDS structure instead of being confined in separate quantum dot. The carrier group velocity components strongly depend both on the mini-band number and the quasi-crystallographic direction. It is interesting to note that in an ideal artificial crystal, it is possible to achieve a very high electron velocity (on the same order of magnitude as the thermal velocity in the host material). This fact is explained by the small size of the quasi Brillouin zone in QDS as compared to the Brillouin zone in bulk crystals. It permits carriers to move easily under the influence of electric field. The latter leads to a much higher conductivity in a regimented quantum dot array compared to that of an array of randomly positioned quantum dots with the same size. Thus the power factor, which is proportional to electrical conductivity, increases leading to \(ZT\) improvement.

Fig. 2 shows electrical conductivity of a three-dimensional regimented p-doped Ge/Si QDS obtained on the basis of model developed in Ref. [6] under certain simplifying assumptions. In our calculations we took into account modification of heavy-hole energy spectrum only.
Figure 2. Electric conductivity at room temperature of simple cubical p-doped Ge/Si QDS with the following parameters: \( L = 2.5 \text{ nm}, \ H = 1.0 \text{ nm}, \ V_e = 0.45 \text{ eV}, \ m^*_w = 0.28 \ m_0, \) and \( m^*_b = 0.49 \ m_0 \) at room temperature as a function of heavy hole quasi-Fermi energy. The depth of potential well is \( V = 450 \text{ meV}. \) The energy in units of eV is counted from the position of the potential barrier. The constant relaxation time value is about \( 10^{-12} \text{ s}. \) Arrows indicate energies when electrical conductivity has local maximum or minimum.

The nonlinear behavior seen in Fig. 2 is explained by slope change of the carrier dispersion branches (changing of the effective sign of major carriers taking part in the conductivity) as quasi-Fermi level shifts up in energy. When quasi-Fermi level is lower then the lowest mini-band, only small part of the tail of Fermi distribution appears in the range of allowed energies. This situation is similar to ordinary conductivity of doped semiconductors and corresponds to quasi-semiconductor conductivity of QDS. When quasi-Fermi energy is inside a mini-band, carries in \( kT \) energy-range almost freely move inside the mini-band over the whole QDS. This corresponds to quasi-metallic conductivity of QDS, which is an order of magnitude larger then that in the quasi-semiconductor regime. The further shifting of the quasi-Fermi energy up to a mini-band gap leads to conductivity drop. This cycle repeats every time as \( E_F \) goes through a mini band. The presented result is valid for the low-field electrical conductivity, when the electronic mini-bands do not split into a Wannier-Stark ladder.

While regimentation of quantum dots makes it easy for carriers to move, phonons are effectively scattered by quantum dots interfaces. The acoustic phonon dispersion in quantum dot superlattices is found from the solution of the elasticity equation (2) by the finite-difference method. Solid lines in Fig. 3 present the phonon dispersion in [[111]] quasi-crystallographic direction. There exist two different types of phonon modes in regimented QDS that emanated from bulk acoustic modes. These modes are quasi-acoustic (\( \omega(q=0) = 0 \)) and quasi-optical (\( \omega(q=0) \neq 0 \)). Quasi-acoustic modes are nothing else but folded acoustic branches of the host material. The multiple reflection of phonons from periodical interfaces leads to a mini-gap formation at the Brillouin zone boundary. The degeneracy due to intersection of different branches is lifted everywhere except for the points of high symmetry. The value of the group velocity for the quasi-acoustic phonons in Ge/Si QDS lies between Si and Ge sound velocities and it is not defined by the volume fractions of two constituent materials. Even in solid alloys where atoms of two materials are randomly distributed elastic properties change almost linearly only in “one-mode behaved” systems such as Na\textsubscript{1-x}KCl. The compositional dependence of phonon energy in Si\textsubscript{x}Ge\textsubscript{1-x} alloy is far from linear. In systems with a spatial regimentation like in 3D regimented QDS the deviation from linear dependence should increase.

Quasi-optical modes correspond to “nearly standing” waves. One can view them as created by periodic scatters such as quantum dot interfaces. These modes can be induced inside quantum dots or in the space between them. A “true” standing wave would have a completely flat dispersion curve, which reflects the fact that this wave does not propagate through the crystal. In contrast, the dispersion branches of quasi-optical modes can have a minimum. The latter means that these modes propagate slowly going back and forth. We refer to these modes as quasi-optical since
they have a nonzero energy in the center of the Brillouin zone, e.g. a cut-off frequency. At the same time one should emphasize that these modes also originate from acoustic bulk phonon modes. The regular optical phonon modes have much higher energy. In Ge/Si QDS of the considered geometry the lowest quasi-optical branch has the energy of about 2.6 meV at the zone center. In bulk Si the longitudinal optical (LO) and transverse optical (TO) phonon energies are $\hbar \omega_{\text{LO}}^\prime = \hbar \omega_{\text{TO}}^\prime = 64.3$ meV. In bulk Ge they equal to $\hbar \omega_{\text{LO}}^\prime = \hbar \omega_{\text{TO}}^\prime = 37.2$ meV. The emergence of many new quasi-optical phonon branches in QDS with low characteristic energy may dramatically modify carrier energy relaxation processes in such structures. For example, along [111] quasi-crystallographic direction (see Fig. 3) the slope of the first hole mini-band is much larger than the phonon group velocity of any branch. It results in scattering suppression in approximately 80% of the Brillouin zone except for the small areas near the center and Brillouin zone boundary.

Inter-mini-band transitions with assistance of one phonon are forbidden for the considered structure. The mini-gap between the first two mini-bands shown in Fig. 3 $E_2 - E_1$ is larger than the optical phonon energy even in the bulk host material. At the same time, multi-phonon scattering in QDC may play a significant role in energy relaxation processes due to the presence of many quasi-optical phonon branches (see Fig. 3). At room temperature, these low-energy branches should have a high population density in accordance with the Bose-Einstein statistics.

Analyzing obtained numerical results we are able to make the following important observation. The existence of 3D mini-bands in quantum dot superlattices may result in nonlinear dependence of electrical conductivity (see Fig. 2), electron part of thermal conductivity, and thermopower (as shown in Fig. 4) on the applied bias. The latter follows from the various possibilities for position of the quasi-Fermi level (QFL) with respect to mini-band edges.

4. CONCLUSIONS

In conclusion, when conditions for mini-band formation are satisfied, carrier transport in such structures can be tuned in a favorable way leading to large carrier mobility, Thermopower, and, as a result, to the thermoelectric figure-of-merit enhancement [6]. To maximize the improvement one has to tune the parameters of quantum dot superlattice in such a way that electrical current is mostly through the well-separated below-the-barrier mini-bands of relatively large width (at least several $k_\text{B}T$, where $k_\text{B}$ is Boltzmann’s constant and $T$ is temperature). Phonon dispersion in 3D QDS is also strongly modified. It affects electron – phonon scattering rates and modifies carrier transport in such structures. On the other hand, existence of multiple periodic scatters reduces phonon part of the thermal conductivity leading to the further enhancement of thermoelectric figure of merit. Modified carrier density of states in 3D regimented QD array result in change of the optical density of states as well. Existence of many low-energy quasi-optical phonons will concur with optical relaxation processes. Thus one may expect very unusual optical spectra in such structures.

This work is supported in part by the by NSF Nanoscale Exploratory Research (NER) program and NSF CAREER Award to A.A.B.

REFERENCES