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The effect of the long-range order in a quantum dot array on the in-plane lattice thermal conductivity

A. KHITUN
Device Research Laboratory, Electrical Engineering Department, University of California - Los Angeles, Los Angeles, California 90095, U.S.A.

A. BALANDIN
Department of Electrical Engineering, University of California – Riverside, Riverside, California 92521, U.S.A.

J. L. LIU, K. L. WANG
Device Research Laboratory, Electrical Engineering Department, University of California - Los Angeles, Los Angeles, California 90095, U.S.A.

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Semiconductor quantum dot superlattices consisting of arrays of quantum dots have shown great promise for a variety of device applications, including thermoelectric power generation and cooling. In this paper we theoretically investigate the effect of long-range order in a quantum dot array on its in-plane lattice thermal conductivity. It is demonstrated that the long-range order in a quantum dot array enhances acoustic phonon scattering and, thus leads to a decrease of its lattice thermal conductivity. The decrease in the ordered quantum dot array, which acts as a *phonon grating*, is stronger than that in the disordered one due to the contribution of the *coherent* scattering term. The numerical calculations were carried out for a structure that consists of multiple layers of Si with layers of ordered Ge quantum dots separated by wetting layers and spacers.

1. Introduction

Quantum dot superlattices (QDS) have recently attracted a lot of attention due to their promise for a verity device applications [1, 2]. Most of the applications envisioned for semiconductor QDS are in the area of optoelectronics [2, 3]. Quasi zero-dimensional (0D) confinement of electrons and holes with corresponding modifications of the density of states allows for artificial re-engineering of optoelectronic properties of such structures. Most recently it was also shown that QDS made of suitable materials can be used for thermoelectric applications [4–6]. Quantum confinement of carriers in QDS adds up to the thermoelectric power, while the additional decrease of the lattice thermal conductivity due to phonon scattering on quantum dots leads to an increase of the thermoelectric figure of merit $\mathrm{ZT} = S^2\sigma_\mathrm{e}/(\kappa + \kappa_\mathrm{e})$. Here, S is the Seebeck coefficient, σ_e is the electric conductivity, κ is the phonon thermal conductivity, and κ_e is the electronic thermal conductivity. It was experimentally found that the thermoelectric power factor of Bi-doped PbT quantum dots array

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structure was higher than that of high quality bulk PbTe. The thermoelectric figure of merit of PbSeTe-based QDS has been shown to be as high as 0.8 at 300 K [6].

These theoretical predictions and preliminary experimental results motivated our present study of thermal properties of the ordered semiconductor QDS. The acoustic mismatch between materials of a quantum dot and that of an surrounding medium (wetting layer or spacer) is expected to produce strong phonon scattering while it does not severely deteriorate electron transport. Thus, QDS may represent a good example of the 'phonon-blocking electron-transmitting' structure. We expect QDS thermoelectric properties to be competing with skutterudite antimonides [7] which have already shown big potential for thermoelectric applications.

Continuous progress in fabrication techniques based on molecular beam epitaxy (MBE) makes possible synthesis of highly ordered arrays of semiconductor quantum dots with both in-plane and vertical correlations [8, 9]. As the size of quantum dots and the inter-dot distance continue to decrease and become smaller than the acoustic phonon mean-free-path Λ, approaching the dominant phonon wavelength λth, the long-range order in quantum dot arrays may significantly alter the phonon transport ($\Lambda = 41$ nm at $T = 300$ K for Si in the Debye approximation and 260 nm in the kinetic theory taking into account the dispersion of phonons [10]). The presence of highly ordered quantum dots may lead to the *coherent* phonon scattering, which significantly enhances the phonon relaxation rate and modifies the phonon group velocity. This paper examines the effects of the long-range order in detail. The rest of the paper is organized as follows. In the next section we describe our theoretical model. In Section 3 we present results of our numerical simulations for a prototype SiGe QDS structure made out of highly ordered arrays of Ge quantum dots separated by Si spacer layers. Our conclusions are given in Section 4.

2. Theoretical model

The expression for the lattice thermal conductivity in the relaxation-time approximation can be written as [11, 12]

$$\kappa = \frac{1}{3}\sum_i \int dk v_{gi}^2(k)\tau_{C_i}(k)S_i(k) \tag{1}$$

where i denotes particular phonon polarization branch, v_{gi} is the phonon group velocity associated with the ith branch, τ_C is the combined relaxation time, $S_i(k)dk$ is the contribution to the specific heat from modes of the polarization branch i in the phonon wavevector interval of kdk. The combined relaxation time τ_C includes all relaxation rates corresponding to the different scattering processes, which do not conserve crystal momentum [12]

$$\frac{1}{\tau_C} = \sum \frac{1}{\tau} = \frac{1}{\tau_M} + \frac{1}{\tau_B} + \frac{1}{\tau_U} + \frac{1}{\tau_D}. \tag{2}$$

Here, $1/\tau_U$ is the three-phonon Umklapp processes, $1/\tau_M$ is the phonon-point defect scattering (isotopes, impurities, etc.), $1/\tau_B$ in the phonon-boundary scattering, and $1/\tau_D$ is the phonon scattering by the quantum dots [4]. Equation (2) includes the phonon relaxation processes, which are dominant in Si, Ge, and Si_xGe_{1-x} Structures. The expressions for phonon relaxation rates $1/\tau_U$, $1/\tau_M$, and $1/\tau_B$ have been derived by Klemens and can be found in Ref. [12].

The new term, which we added $1/\tau_D$, will be treated here in detail. The most general expression for the phonon scattering rate on quantum dots can be written as

$$\frac{1}{\tau_D} = \frac{v_g \sigma_v}{V} \tag{3}$$

where σ_V is the total cross section of the dot ensemble of volume V. Due to the fact that the characteristic feature size of a quantum dot is smaller than the phonon mean-free-path and approaches the phonon coherency length ($L \sim 2$ nm [10]), the phonon relaxation on quantum dots has to be considered as a separate scattering

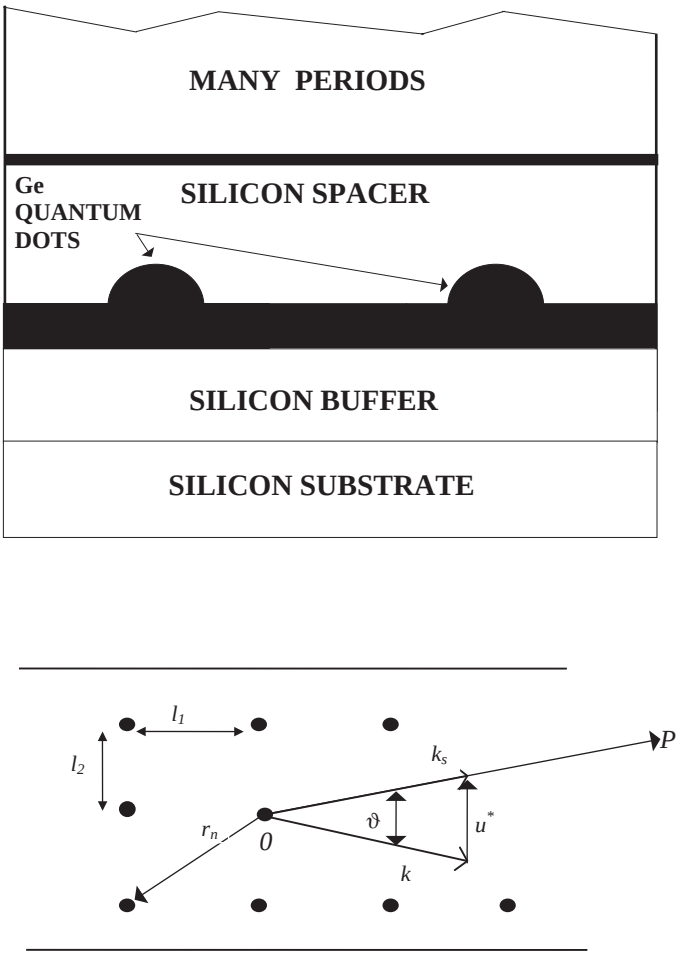

Fig. 1. Schematic view of the SiGe quantum dot superlattice (QDS).

process. In this work we treat all dots as equal regimented semi-spheres with radius a on a plane, which is perpendicular to the growth direction, as shown in Fig.1. The spacer layer is assumed to be rather thick ($\sim$100 nm) so that we may disregard phonon spatial confinement effects. To describe the phonon transport in QDS, we use the continuum model approximation and an assumption that the thermal phonon wave can be represented by a sum of plane waves [4]. Thus, the expression for the scattering cross section σ of a single quantum dot becomes [13]

$$\sigma = \frac{\pi}{k^2} \sum_{m=0}^{\infty} (2m+1)|1+R_m|^2. \tag{4}$$

Here R_m is a reflection coefficient

$$R_m = \frac{h_m'^*(ka) + i\beta h_m^*(ka)}{h_m'(ka) + i\beta h_m(ka)} \tag{5}$$

where $\beta = i\frac{\rho C}{\rho_e C_e}\left[\frac{j_m'(ka)}{j_m'(k_e a)}\right]$, ρ is the density, c is the sound velocity, the subscript e denote the parameter of

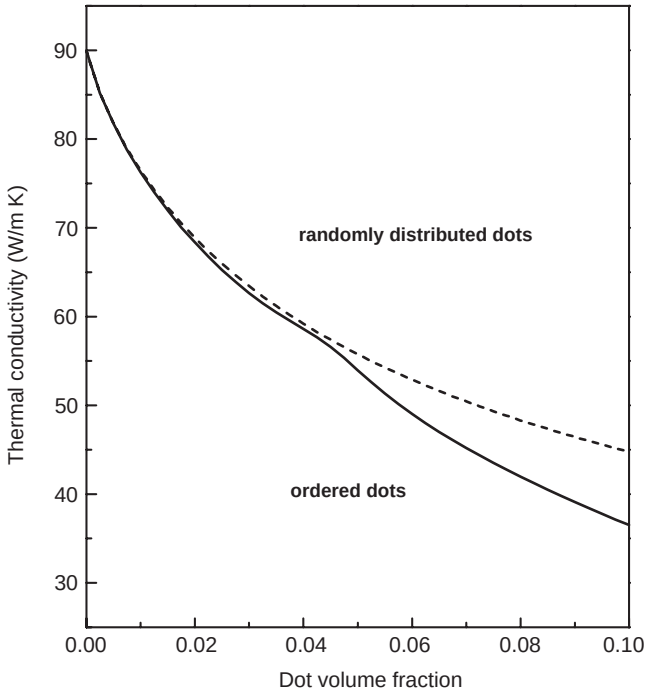

Fig. 2. In-plane lattice thermal conductivity of the SiGe quantum dot superlattice based on the *ordered* quantum dot arrays (solid line), and on the *disordered* quantum dot arrays (dashed line) as functions of the volume fraction of quantum dots. The results are shown for $a = 6$ nm, and $T = 300$ K.

the dot material, $h_m(ka) = j_m(ka) + iy_m(ka)$, j and y are the spherical Bessel functions of the first and second kinds, respectively, and h_m^* is the complex conjugate. In the long-wave and short-wave limits, eqn (4) simplifies to $\sigma \sim 5.6(ka)^4a^2$ for $ka \ll 1$; and $\sigma \sim 2\pi a^2$ for $ka \gg 1$, respectively. One can see from these limits that the phonon scattering on the quantum dots is an intermediate process between the point defect and the boundary scatterings. A quantum dot acts as an impurity atom in one limit if the dot size is much less than the phonon wavelength. In the other limit, when the dot size is much larger than the phonon wavelength, a quantum dot acts as an additional boundary.

In order to find σ_V, we have to sum the contributions from all scattered waves from all the dots. At some arbitrary point P (see Fig. 1) the reflected amplitude S normalized to the amplitude of the incident plane wave is given as

$$S = \frac{|F(\vartheta)|^2}{r^2}\left[N + \sum_{n\neq m} e^{(iu^* r_{nm})}\right] \tag{6}$$

where the scattering function $F(\vartheta)$ is

$$F(\vartheta) = \frac{i}{2k}\sum_{n}^{\infty}(2n+1)(1+R_n)P_n(\cos\vartheta) \tag{7}$$

and $P_n(\cos\vartheta)$ are Legendre polynomials, where $u = k_0 - k$, k and k_0 are the wavevectors of the plane and scattered waves (see Fig. 1). The sum in eqn (6) is split into two terms

$$\left[N + \sum_{n\neq m} e^{(iu^* r_{nm})}\right]. \tag{8}$$

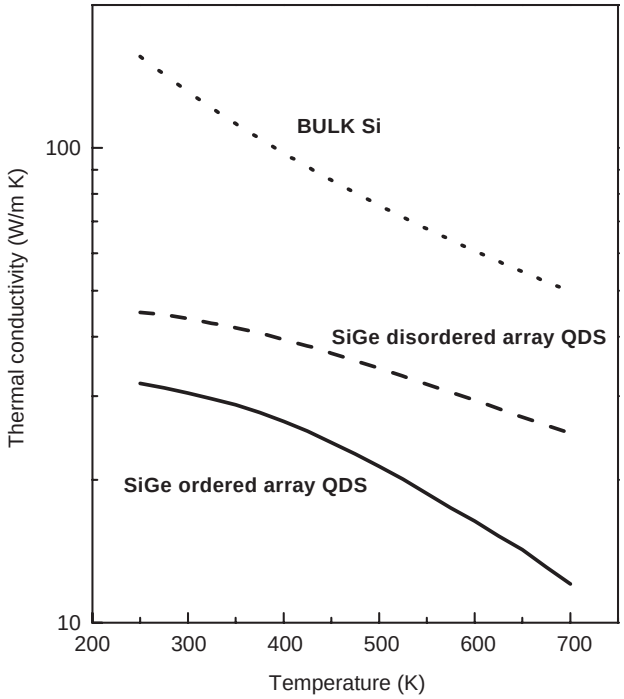

Fig. 3. In-plane lattice thermal conductivity as a function of temperature for the Si/Ge QDS based on the ordered quantum dot arrays (solid line), on the disordered quantum dot arrays (dashed line), and for bulk Si (dotted line). The results are shown for $\delta = 0.1$, $a = 6$ nm, and $T = 300$ K. The bulk Si thermal conductivity result is after Balandin and Wang [16].

The first term on the right-hand side of eqn (8) is the number of dots in volume V and represents the scattering of phonons from quantum dots when they act as independent scattering centers. We refer this to the *incoherent* scattering term. The second term on the right-hand side of the eqn (8) represents the cooperative scattering action of the quantum dots. We refer this to the *coherent* scattering term, in analogy with the terminology adopted in acoustics [13].

It is important to note that if the dots are randomly distributed, and the total reflected intensity is small in comparison with the incident one, the coherent term in eqn (8) vanishes. In this case, the total scattering cross section of the quantum dots can be approximated by a scattered cross section sum of single dots $\sigma_v \approx N\sigma$. In the case of regimented quantum dots, which is equivalent to the in-plane long-range ordering for our structure, the intensity of the scattered waves will add in some directions, thus generating diffraction beams. As a result, the quantum dot superlattice will act as a *phonon grating*. The angle distribution of the diffracted beams will be determined by the periods (l_1, l_2) of the in-plane quantum dot distribution (see Fig. 1).

In this paper we restrict our analysis to the effect due to the case of regimented QDS, in terms of the coherent scattering term, on the in-plane lattice thermal conductivity of QDS. The integrated effect of the coherent term in the long-wavelength limit will manifest itself via a particular dependence of the scattered intensity on the number of quantum dots. It can be shown [13] that the scattered intensity is proportional to the *square* of the number of the scattering centers per unit volume V. Thus, for the ordered quantum dot array, we have $\sigma_V \sim N^2$, while for the disordered quantum dot array, $\sigma_V \sim N$ (see eqn (8)). This *quadratic* dependence of the scattering cross section σ_V on the number of quantum dots may increase the relaxation of the acoustic phonons, which help carry most of heat in such technologically important semiconductors as Si, Ge and SiGe.

In the forward direction the increased phonon scattering modifies the phonon dispersion in such a way that acoustic phonons travel with a group velocity different from the one in bulk. The problem of the wave dispersion in a medium containing a number of scatters has been intensively studied for a long time [14, 15]. In this work we adopt an expression for the modification of the wavenumber k due to scattering derived by Lax [15],

$$\left(\frac{k'}{k}\right)^2 = 1 + \frac{4\pi\zeta F(0)}{Vk^2} \tag{9}$$

where k' is the wavenumber in the presence of quantum dots, k is the wavenumber in the absence of the dots, ζ is the constant expressing the ratio of the exciting field to the total field $\zeta = F_{\text{total}}/F(0)$ [15], $F(0)$ corresponds to the forward scattering. This formula was derived under assumption that the concentration of quantum dots (N/V) is low, so that the influence of the backward scattering, which is proportional to $(N/V)^2$, can be ignored. For the randomly distributed quantum dots, under the assumption of weak scattering, we have $\zeta = 1$. For the ordered quantum dot array, the parameter ζ becomes proportional to N [15]. The latter can be explained in terms of the coherent and incoherent scatterings. Thus the phonon modification, caused by the scattering on dots, results in a decrease in phonon group velocity $\upsilon_g = |\partial\omega/\partial q'|$. Since the acoustic phonon relaxation rate strongly depends on the phonon group velocity [16, 17], one can expect a strong modification of the lattice thermal conductivity in the regimented quantum dot arrays. Additional decrease of the acoustic phonon group velocity may come from the spatial confinement of phonon modes inside the two-dimensional spacer and wetting layers of QDS [16]. But as it was mentioned earlier, we restrict our analysis to the QDS with rather wide Si spacer layers so that we neglect the influence of phonon confinement and only consider modification of the group velocity due to scattering on regimented quantum dots, e.g. phonon grating.

3. Results and discussion

Numerical calculations have been carried out for SiGe QDS with the spacer layer of 100 nm at temperature 300 K and $a = 6$ nm ($\rho = 2.33 \times 10^3$ kg m^{-3}, $c = 8.47 \times 10^5$ cm s^{-1}, $\rho_e = 5.32 \times 10^3$ kg m^{-3} and $c_e = 4.52 \times 10^5$ cm s^{-1}). The calculation procedure runs as follows. First, we calculated the scattering function using eqn (7), the reflection coefficient using eqn (5) and the scattering cross section of a single quantum dot (eqn (4)). Second, using eqn (9), the phonon dispersion and modified phonon group velocity were found. Next, we calculated the phonon relaxation rates and the lattice thermal conductivity κ (eqn (1)). The overall procedure of calculation of the in-plane lattice thermal conductivity was analogous to the previous reported by us for the case of quantum wells [16, 17] and quantum wires [18].

Figure 2 presents the results of numerical calculations of the in-plane lattice thermal conductivity of SiGe QDS as a function of the volume fraction of Ge quantum dots. The dashed line depicts the in-plane lattice conductivity of SiGe QDS with randomly distributed quantum dots, while the solid line shows the thermal conductivity of the ordered quantum dot array. The difference of thermal conductivity is caused by the additional *coherent* term, which is responsible for the enhancement of the acoustic phonons scattering in the *ordered* QDS. As it seen in Fig. 2, the difference becomes significant as the dot volume fraction (number of quantum dots per unit volume) increases to about 0.06. At the volume fraction of 0.1, the decrease is about 30% of the value of the in-plane thermal conductivity of the *random* quantum dot array. It is interesting to note that the onset of deviation of the thermal conductivity of the ordered array from that of the random dot array starts at the volume fraction of about 0.05, which approximately corresponds to the inter-dot distance equal to the dot diameter.

In Fig. 3, we present the in-plane lattice thermal conductivity of the SiGe QDS as a function of temperature (up to 700 K). The results are presented for the ordered quantum dot array (solid line) and disordered quantum dot array (dashed line). For comparison, the Si bulk thermal conductivity is also shown by the dot-

ted line. These results are for the particular case with $\delta = 0.1$, $a = 0.6$ nm, $l_1 = 8a$ and $l_2 = 6a$. It is interesting to note that the difference in the lattice thermal conductivity for the *ordered* and *disordered* arrays remains significant in a wide temperature range. The latter is particularly important for thermoelectric applications since SiGe bulk alloys and low-dimensional structures have been shown to be good high-temperature thermoelectric [19].

4. Conclusions

We have theoretically investigated the in-plane lattice thermal conductivity of the ordered arrays of quantum dots. It was shown that the long-range ordering of the quantum dot array enhanced acoustic phonon scattering and, thus led to a decrease of its lattice thermal conductivity. The decrease in the ordered quantum dot array was stronger than that in the disordered one due to the contribution of the *coherent* scattering term. For some realistic Si/Ge quantum dot array parameters, we found that the regimentation of the quantum dots might lead to an additional decrease of the lattice thermal conductivity (30% for the quantum dot volume fraction $\delta = 0.1$). This decrease was caused by the coherent acoustic phonons scattering. The strength of this effect depended on the volume fraction occupied by the quantum dots and the acoustic mismatch between the material of quantum dots and the spacer layer. The obtained results are important for recently suggested high-temperature thermoelectric applications of the QDS that consist of the *ordered* quantum dot arrays.

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