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Thermal transport within quantum-dot nanostructured semiconductors

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ABSTRACT

In this work, we aim at exploring the effects of the germanium quantum dot (QD) layer embedded in silicon thin films on the thermal transport property in use of the non-equilibrium molecular dynamics simulation tool. An attempt is made to distinguish and understand the effect of the QDs themselves and the effect of the wetting layer on which QDs are grown. In this study, we notice as often observed a significant increase in the thermal resistance due to heterogeneous interfaces. Moreover, it is found that a simple QD interface has a thermal resistance monotonically decreasing with increasing quantum dot density. It is probably because the QDs make the transition from one material to another smoother, alleviate the acoustic mismatch, and thus assist the energy transport. When the germanium QDs together with a germanium wetting layer is inserted into a silicon material, the involved interface thermal resistance decreases first but increases later with increasing quantum dot density. The competition between the roughness effect and the wave interference effect is employed to explain this variation trend. As far as the quantum-dot superlattice thin film is concerned, we find its effective thermal conductivity decreases monotonically with increasing quantum dot density and with decreasing film thickness. In all cases, the size of quantum dots affects little on the thermal resistance/conductivity.

1. Introduction

For the past two decades, low-dimensional materials such as thin films and nanowires have attracted a lot of attention because of their potential capability in raising the figure-of-merits of thermoelectric materials [1–6]. Nanocomposites [7], usually fabricated by hot pressing nano- and/or micro- particles, and nanostructured alloys [8,9] are two other potential thermoelectric materials. In spite of relatively low cost, they are not necessary superior to the low-dimensional materials because their power factors are usually deteriorated at the same time as their thermal conductivities are reduced by the interface/grain boundary scatterings. Nanoprecipitates either embedded in the grains or located at the grain boundary have been found useful in enhancing the electric conductivity and consequently improving the power factor [10–12]. Theoretical as well as experimental investigations [13–16] further found that zero-dimensional structures such as quantum dot superlattice (QD superlattice) improve the thermoelectric efficiency even more. It is generally believed that the quantum dots not only enhance the power factor by modifying the electron energy band structure through the strong confinement effect but also reduce the thermal conductivity by inducing additional scatterings. The latter nonetheless is not so clearly understood and has become the motivation of the present study.

In understanding the effect of QDs on the lattice thermal conductivity, few theoretical investigations have been built, mostly based on the Callaway-Klemens model under the relaxation time approximation in which the quantum dot effect was modeled as an additional scattering mechanism [17–19]. Taking the disordered interface conditions into consideration, Shamsa et al. [19] proposed a phonon-hopping model and calculated the thermal conductivity of QD superlattices based on a phonon-transport-resistance network. Their analysis shows the thermal conductivity of QD superlattices decreases with the decreasing QD size. Liu et al. [17] fabricated samples by a solid source molecular beam epitaxy (MBE) system and measured the cross-plane thermal conductivity of Si/Ge–QD superlattices with Ge content from 7% to 20% and a Si spacer of 20 nm by the 3 ω method. They found that the thermal conductivity is significantly reduced compared with the bulk values of Si and Ge and a scattering rate derived based on the total cross section of the dot ensemble predicts well with the measurements. Bao et al. [15] reported that in the low-temperature region, the thermal conductivity is proportional to $T^{0.7}$–$T^{0.9}$. Yang et al. [20] studied the nano-dot superlattices with a period of 7.5 nm and extracted a thermal conductivity of 2.92 W/m K. Measurements of Lee and Venkatasubramanian [21] revealed that the cross-plane thermal conductivity of the Si/Ge–QD superlattices grown by the low-pressure chemical vapor deposition decreases monotonically with decreasing period and with increasing nano-dot areal density and reaches values lower than those in typical SiGe alloys (6.5 W/m K). Alvarez-Quintana et al. [22] used a seed layer of C to

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counteract stress memory between layers in order to adapt the degree of vertical correlation of the dots. They found at least a twofold decrease of the cross-plane thermal conductivity in uncorrelated dot structures as compared to structures with the same Si spacer of 20 nm but good vertical dot alignment. The observed impact of disorder on the conductivity provides an alternative route to reduce the thermal conductivity of QD superlattices.

To embed QDs in some host material, a thin layer, called the wetting layer, is usually grown first and cone-like QDs are next grown on it. For instance, in the $PbSexTe_{1-x}$/PbTe–QD superlattices fabricated by Harman et al. [13], $PbSe_{0.98}Te_{0.02}$ spontaneously grew in the form of QDs after the growth of a 0.6- to 0.7-nm-thick wetting layer. The height-to-base aspect ratio was about 1:3 and the QD density was on the order of 10^{11} QDs/cm^2. The wetting layer thickness of the Si/Ge–QD superlattice of Liu et al. [17] was 1–2 nm. The characteristic size of the Ge–QDs is 100 nm in base and 10 nm in height. Bao et al. [15] estimated, based on the SEM and AFM results, an average base diameter of 40 nm and a height of 4 nm for their Ge–QDs. It has not been investigated however whether the thermal conductivity reduction is attributed to the existence of the QDs or the wetting layer or both. The answer can not be easily obtained via either theoretical analyzes or experimental measurements. In this work, we attempt to perform the non-equilibrium molecular dynamics (NEMD) simulations to find the answer.

The MD simulation starts from selecting a proper interatomic potential and setting up the initial positions and velocities of atoms. The atomic trajectories are then traced according to the Newton's second law. This numerical method has been widely utilized for many nanoscale applications, such as in exploring the mechanical or thermal properties of nanostructures [23–25]. For analyzing thermal properties, there are two kinds of MD methods, the equilibrium MD (EMD) and the non-equilibrium MD (NEMD). In the EMD approach, the thermal conductivity is calculated based on the fluctuation-dissipation theorem or the Green-Kubo relation. In NEMD approaches, either a constant heat flux or constant boundary temperatures are imposed, the temporally averaged temperature gradient is next calculated, and finally the thermal conductivity is obtained by applying the Fourier's law. A comparison between these two approaches can be found in the work of Schelling et al. [26]. In spite of its wide applications, there are few literatures applying the MD techniques to the thermal-conductivity study of QD embedded materials. Using EMD, Kawamura et al. [27] calculated the thermal conductivity of AlN/GaN–QD superlattices in which the GaN–QD had a trapezoid shape. A minimum cross-plane thermal conductivity was found as the spacer thickness was 2 nm.

In this work, we design three different heterogeneous structures in order to clarify the QD effect on the lattice thermal conductivity. The first one connects a silicon thin film and a germanium thin film with a plane interface on which Ge–QDs are grown. These QDs are like "regular roughness" of the interface and make a gradual transition from silicon to germanium. Unfortunately, due to the limitation of the computational capability of modern computers, only small-sized systems can be simulated and therefore QDs much smaller than the actual ones can be embedded. The QD size investigated herein is only a few nanometers in base and height and for simplicity each QD is simplified as a square pyramid. The second structure inserts a Ge–QD layer together with a wetting layer in the middle of a silicon thin film. The goal is to distinguish the influence of the wetting layer from that of the QDs alone by comparing the simulation results of the first and the second layouts. The last layout is the Si/Ge–QD superlattice thin films. The effects of the QD density and the spacer thickness on the lattice thermal conductivity of the QD superlattice thin films are targeted.

2. Problem description and simulation tool

Fig. 1 illustrates the three heterostructures to be investigated. The shape of the QDs is a square pyramid having a base area of $\ell \times \ell$ and a height of h, as also shown in Fig. 1. The wetting layer, if exists, has a fixed thickness of 1UC (unit cell). Two QD sizes are investigated: (ℓ, h) = (2UC,1UC) and (4UC,2UC). The QD density (δ_{QD}) is defined as $N\ell^2$, where N is the number of QDs per unit cross sectional area. A heat flux perpendicular to the interface(s) is desired and periodic boundary conditions are employed in the other two directions.

In the NEMD simulations, we employ the Stillinger-Weber potential and the widely used mixing rules [26] to describe the interaction among Si and Ge atoms. A system similar to that studied by Landry and McGaughey [28] is built. Two thermal reservoirs are added at the ends of the simulated sample. Each of them has a thickness of 12UC and has its temperature or total energy controlled by the velocity rescaling technique [29]. A 2UC-thick layer of fixed atoms is attached to the outer side of each reservoir in order to prevent reservoir atoms from evaporation/distortion. The cross section of the simulated samples is 4UC × 4UC or larger, selected in such a way that an integer number of QDs are always simulated as the QD density varies. Instead of a NPT system which is stress-free, NVE systems are adopted in the present study. Initially the silicon and germanium lattice constants are used along the z-direction in the silicon and germanium regions respectively but the average one weighted by the numbers of silicon and germanium atomic planes is adopted in the periodic directions [30]. The system is then kept equilibrium at a prescribed initial temperature for a while before a heat flow is evoked in the system. Fig. 2 shows the test results of a simple system which consists of a 100UC–Si film and a 100UC–Ge film in connection by a perfect plane interface (without QDs). As seen, the equilibrium lattice constants in the Si and Ge regions are very close to those obtained from the NPT systems [31] and the equilibrium lattice constant at the interface is just the average of the Si and Ge equilibrium lattice constants. The system temperature according to the classic definition (proportional to the kinetic energy of the system) is set to be as high as 500 K so that the temperature quantum correction is minor and can be omitted.

To generate a heat flux in the system, both the controlled-heat-flux method and the controlled-temperature method are attempted. In the former, a fixed amount of energy ($\Delta\varepsilon$) is added/extracted into/from the hot/cold thermal reservoir at every time step; in the latter, the kinetic energies of the reservoirs are maintained constant. In both methods, the velocities of atoms in the reservoirs are rescaled accordingly with the velocity of the mass center keeping unchanged [29]. Simulations of the simple system mentioned above show that the temperature distribution converges quickly in either method ($\Delta\varepsilon = 2 \times 10^{-4}$ eV or T_H = 530 K and T_C = 470 K, where T_H and T_C are the controlled temperatures of the hot and cold thermal reservoirs respectively). However, a measure of the heat flux along the z direction shows large oscillations as shown in Fig. 3. The finite length of the system seemingly causes an energy wave bouncing back and forth in between the reservoirs, resulting in a very slow convergence. The situation is worse in the heat-flux-controlled method than in the temperature-controlled method. Fig. 4 shows at least 12 million time steps are required to obtain an approximately constant average heat flux. The thermal resistance of the perfectly smooth interface is found to be 2.5×10^{-9} m^{2}K/W (controlled-heat-flux method) and 2.67×10^{-9} m^{2}K/W (controlled-temperature method), close to $2.7 \pm 0.2 \times 10^{-9}$ m^{2}K/W obtained by Landry and McGaughey [28] and 2.85×10^{-9} m^{2}K/W predicted by Zhao et al. [31] using the lattice dynamics method.