Growth of Ge quantum dot superlattices for thermoelectric applications

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Abstract

We report on the thermal conductivity measurement of Ge quantum dot superlattices. The samples used were grown using molecular beam epitaxy. The typical dot sizes were determined by transmission electron microscopy measurements to be 75 nm in base and 7 nm in height. A differential $\Delta T$ method was employed to characterize the thermal conductivity of the samples. At room temperature, thermal conductivity was determined to be 6.2 and 30.5 W/mK in the cross-plane and in-plane direction, respectively. Temperature-dependent measurements showed that cross-plane thermal conductivity monotonously decreased while in-plane thermal conductivity showed a peak as the temperature decreased from 300 to 80 K. The results were well explained using a model based on the Boltzmann transport equation for cross-plane conductivity and based on the relaxation time approximation by including phonon scattering by quantum dots for in-plane thermal conductivity. © 2001 Elsevier Science B.V. All rights reserved.

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Thermoelectric materials with high figure of merit can enable novel thermoelectric and thermionic devices with efficient solid-state refrigeration and power conversion. In recent years, there has been a considerable interest in exploiting the thermoelectric properties of low-dimensional structures, such as quantum wells [1,2], superlattices [3,4] and one-dimensional wires [5,6]. These studies demonstrate that the low-dimensional structures have higher figures of merit due to their higher thermoelectric power and lower thermal conductivity compared with their bulk constituent materials or equivalent composition alloys. Zero-dimensional quantum dot structures, however, might have even greater potential in thermoelectric applications. Firstly, it was found that quantum dots might effectively confine phonons [7] or could even strongly scatter phonons [8], which result further in their thermal conductivity reduction. Meanwhile, quantum dots
have δ-like density of states and quantum confinement of electrons (holes) could also add up to the additional improvements of the thermoelectric power factor and the figure of merit. Thus, quantum dot may represent a better example of the “phonon-blocking electron-transmitting” structures compared with alloys, quantum well superlattices and wires. In fact, thermoelectric figure of merit enhancement has been demonstrated in the Bi-doped SbTe quantum dot system [9].

Self-assembled Ge quantum dots can be formed during the epitaxial growth of Ge on Si due to the 4.16% lattice mismatch between them. Interband and intersubband properties of Ge quantum dots have been studied for the development of novel quantum dot lasers and detectors [10,11]. In addition, well-arranged dot arrays were studied for possible applications in the information processing [12]. It was expected that Ge quantum dots might have new applications in the thermoelectrics due to the above reasons.

In this paper, we report experimental results on the thermal conductivity reduction in Ge quantum dot superlattices. Samples were grown by solid-source molecular beam epitaxy (MBE). The substrates were p-type Si (100) wafers with resistivity of 15–30 Ω cm. The growth temperature was kept at 540°C and the growth rates were 1 and 0.2 Å/s for Si and Ge, respectively. Two samples used in this experiment consisted of 10 bi-layers and 50 bi-layers, in which Ge quantum dot layers were separated by 20-nm-thick Si spacer layers. Each Ge quantum dot layer was formed by the self-assembly via the Stranski–Krastanov growth mode with deposition of 15 Å Ge. The structure characterization was performed using a Hitachi-9000NAR high-resolution electron microscope (HREM) with point-to-point resolution of 0.18 nm. Fig. 1 shows a typical cross-sectional HREM image of the 10-period sample. The typical dot base diameter and height were determined by many of these images to be 75 and 7 nm, respectively. The dot density and nonuniformity were obtained by atomic force microscopy (AFM) to be $2 \times 10^9$ cm$^{-2}$ and 19%, respectively, by scanning over the surface after the first Ge layer growth.

The thermal conductivity of the quantum dot superlattice was measured by a differential 3ø method [13,14]. In this method, a 100-nm SiN$_X$ film was first deposited on the superlattice and an identical substrate (a reference sample). The reason to introduce the SiN$_X$ layer is to avoid the current leakage into the superlattice film and the reference sample during the measurement. Metal wires were then deposited onto the SiN$_X$ films to act as both heaters and temperature sensors. The temperature drop across the superlattice film was obtained by the difference of the temperature rises of the metal wires on the two samples. Thermal conductivity can be determined by the following expression [14]:

$$\frac{\Delta T}{q} = f(\kappa_X, \kappa_Y, \kappa_S, \kappa_{SiN}, d_1, d_2, b),$$

where $\Delta T$ is DC temperature drop across the quantum dot superlattice film, $q$ is the heat flux through the heaters, $f$ is a complicated integral function [4] that depends on the thermal conductivity.
conductivity (in-plane: \(k_x\), cross plane: \(k_y\)) of the quantum dot superlattice film, the substrate thermal conductivity (\(k_S\)), the insulation film thermal conductivity (\(k_{SiN}\)), the superlattice film thickness (\(d_1\)), the insulation layer thickness (\(d_2\)), and the metal wire width (\(b\)). Fig. 2 shows the temperature rises in the reference and the 10-period quantum dot superlattice sample as functions of modulation frequencies. In this experiment, heater wire width is 10\(\mu\)m and the input power is 26.5 mW. The measurement was performed at 300 K. The temperature drop across the superlattice film was 0.133 K, constant over a wide frequency range and was equal to the DC temperature difference. The cross-plane thermal conductivity is then determined to be 6.2 W/mK. This thermal conductivity value of the Ge quantum dots is almost one order of magnitude lower than that of the bulk Ge (\(\sim 60\) W/mK). For comparison purpose, the equivalent Ge fraction of the Ge quantum dot sample was estimated to be 7\%. The thermal conductivity of an undoped Si\(_{0.95}\)Ge\(_{0.05}\) alloy is about 12 W/mK [15], or twice as that of the thermal conductivity of the Ge quantum dots.

It is important to note that the lowest cross-plane thermal conductivity of a SiGe-based structures reported so far is 1.2 W/mK [16]. This SiGe sample consisted of 100-period, Sb-doped, symmetrically strained Si (20 Å)/Ge (20 Å) superlattice on top of a 1.3-\(\mu\)m-thick SiGe graded buffer grown on a SOI substrate. The low thermal conductivity obtained could be due to the efficient phonon confinement and/or phonon scattering at the interfaces, dopants and threading dislocations. The disadvantage of this structure is that the electrical conductivity is very low due to the presence of high-density dopants (\(2 \times 10^{18}\) cm\(^{-3}\)) and threading dislocations (\(1.5 \times 10^8\) cm\(^{-2}\)). Moreover, the indispensable thick buffer layers for the formation of high-quality, symmetrically strained superlattices prevent them from any serious thermoelectric application. For the present quantum dot superlattice, however, the electron transport does not degrade because the structure is dislocation free. In addition, it is expected that much lower thermal conductivity can be obtained for quantum dot superlattices if one increases the number of interfaces per unit length in the growth direction by reducing the thickness of the Si spacers.

Fig. 3 shows the measured cross-plane thermal conductivity of the 10-period quantum dot sample as a function of temperature. The scattered
squares are experimental data while the error bars represent the experimental uncertainty of the thermal conductivity, arising from the data measured with metal wires of different sizes. The thermal conductivity decreases with decreasing temperature ranging from 300 to 80 K. To explain the experimental data, we used a model based on the Boltzmann transport equation for the cross-plane direction [17]. The model employed an interface specularity parameter “p” to represent the fraction of phonons experiencing specular reflection/transmission at the interface while the rest of phonons undergo a diffuse process. In the quantum dot superlattice case, the “roughness” of the two interfaces in one superlattice period is not the same and should not have the same “p” parameter. In simplicity, we used the average thickness of the Si (200 Å) and Ge (15 Å) layers and a chosen “p”. The solid line in Fig. 3 is the calculation result fitted by $p = 0.45$. The relatively small value of the fitted specularity parameter ($p = 0.45$) indicates “rough” interfaces. The trend that the cross-plane thermal conductivity increases with the increasing temperature is because of that interface reflection always reduces the heat flow.

In order to obtain in-plane thermal conductivity of the Ge quantum dots, a relatively thick film, namely 50-period Ge quantum dot superlattice was prepared. Moreover, a relatively small width heater was used so that it could create a larger heat spreading in a small region in the in-plane direction of the film. As a matter of fact, two wires, namely, 2 and 30 μm in width were used in this work. The measured temperature rises across the film were used to find the in-plane thermal conductivity through the above-mentioned two-dimensional heat conduction modeling. This method (2 wires $3\omega$ method) has been successfully used to characterize thermal conductivity of Si/Ge short-period superlattices [14]. Fig. 4 shows the temperature measured at 300 K for 2 and 30 μm width heaters deposited on the reference and the 50-period quantum dot superlattice sample. The in-plane thermal conductivity was determined to be 30.5 W/mK.

Fig. 5 shows the in-plane thermal conductivity as a function of the substrate temperature. In contrast to the temperature dependent cross-plane thermal conductivity, the in-plane thermal conductivity increases slightly as the temperature decreases from 300 K to about 110 K. When the temperature decreases further, the conductivity decreases drastically. This phenomenon may be explained using a relaxation-time approximation. In this model, the in-plane lattice thermal
conductivity is written as [18]

\[
\kappa = \frac{1}{3} \sum_i dk \nu_{gi}^2(k) \tau_C(k) S_i(k),
\]

where \(i\) denotes a particular phonon polarization branch, \(\nu_{gi}\) is the phonon group velocity, \(\tau_C\) is the combined relaxation time, \(S_i(k)\) is the contribution to the specific heat from modes of the polarization branch \(i\) with the phonon wave vector interval of \(kd\). Thermal resistance or conductivity arises due to phonon relaxation in different scattering processes that do not conserve crystal momentum [19]. In general, the scattering processes which are dominant in crystalline Si_{1-x}Ge_{x} include three-phonon Umklapp processes, point defect scattering (isotopes, impurities, etc.) and boundary scattering. For the present quantum dot sample, a new phonon relaxation mechanism, namely, scattering by quantum dots, should also be included. As the characteristic feature size of a quantum dot becomes smaller than the phonon mean-free-path \(\lambda\), approaching the phonon coherence length \((\lambda \sim 2 \text{ nm})\), phonon relaxation by quantum dots has to be invoked as a separate scattering process. The phonon scattering rate by quantum dots is \(1/\tau_D = \nu_g \sigma_v / V\), (where \(\sigma_v\) is the total phonon scattering cross section in volume \(V\) and \(\nu_g\) the phonon group velocity modified by scattering on quantum dots) [8]. The calculation result is shown in Fig. 5 (solid line) and it has the same trend as the experimental data, indicating that the temperature dependence of in-plane thermal conductivity can be well explained by the relaxation-time approximation.

In summary, we have studied thermal conductivity properties of quantum dot superlattices. Thermal conductivity was determined to be 6.2 and 30.5 W/mK at 300 K in the cross-plane and in-plane, respectively, for our specific dot superlattices. The temperature dependence was also studied. These results suggest that Ge quantum dot structure is a promising candidate for thermoelectric applications.

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References