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Quantum Size Effects on Phonon Transport in Ge Quantum Dot/SiO_2 System

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1. Introduction

Nanoparticles inclusion into thermoelectric (TE) materials has been experimentally demonstrated to be an approach for reducing the thermal conductivity below that of the simple host medium [1, 2], but also theoretically predicted to pave the way for enhancing the power factor above that of the host via electron filtering [3]. This suggests that nanoinclusion may provide a promising solution for the dilemma of bulk TE materials because of competing effects of electrical and thermal conductivities and open up an accelerated way for boosting the figure of merit (ZT) of TEs. Motivation to study Ge quantum dots (QDs)/SiO_2 system is strong in light of the lower bulk Ge thermal conductivity (k), higher electrical conductivity (σ), similar Seebeck coefficient (S) in comparison with Si, and in particular, the compatibility to Si integrated circuit (IC) technology. This suggests that Ge nanostructures should have better TE efficiency and may present advantages on enabling efficient site-specific cooling as well as solutions for eliminating parasitic interface thermal resistances in integrating TE materials onto IC chips.

The authors have developed a self-assembled method for the generation of Ge QDs through thermal oxidation of $Si_{1-x}Ge_x$-on-insulator (SGOI) structures, and demonstrated self-organized stacked Ge QDs in SiO_2 or Si_3N_4 arrays with well placement in large quantity [4, 5]. This approach may offer some advantages over the epitaxial growth for stacked QD multilayer system, in which a maximum stacking number is set by the overall accumulated homogeneous strain with an increase in the number of QD stacks. Additionally the proposed Ge QDs systems are produced by thermal oxidation and thus are thermal stable at least up to 900 ^{o}C without possible concerns of intermixing and strain relaxation. This experimental demonstration of Ge QDs arrays is readily transferable for incorporating them with existing silicon PV and TE structures.

2. Experimental

In this paper, temperature-dependent thermal conductivity, $k(T)$, of various sized (4.9-, 6.3- and 7.6 nm) Ge QDs embedded in SiO_2 (Fig. 1) were evaluated in terms of thin film resistance thermometry using a single metal-line as both the heater and thermometer. A steady current is applied through contact pads and the resulting voltage change is monitored using four-point-probe technique. Bulk Ge, Si, and SiO_2 are also characterized for comparison.

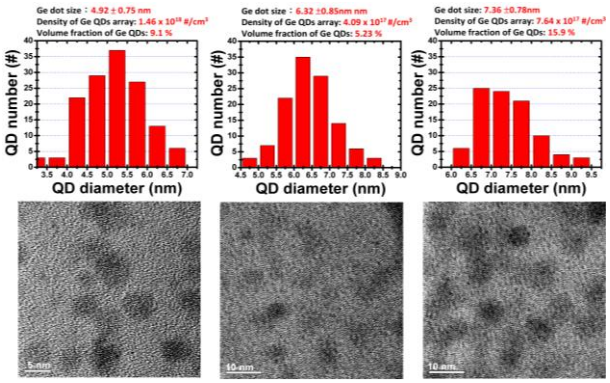

Fig.1 Cross-sectional TEM images of studied Ge QDs and the corresponding QD size distribution, average size, density, and volume fractions in SiO_2.

3. Results and Discussion

There appear enormous difference in magnitude and considerable deviation on temperature dependence of thermal conductivity between Ge QDs/SiO_2 system and bulk Ge or SiO_2, and such distinctions become evident as the QD diameter gets smaller. Figure 2(a) illustrates $k(T)$ curves of 4.9-, 6.3- and 7.6 nm-Ge QDs/SiO_2 samples all alighting well below the ones for bulk Ge and SiO_2 with a respective 200- and 2–5 fold of magnitude lower than the corresponding bulk values. An effective media model (EMM), which takes account of the temperature-dependent thermal conductivity of bulk Ge and SiO_2, the volume fraction of Ge QD in the oxide matrix, and the thermal interface resistance between Ge QDs and SiO_2, is employed to numerically calculate effective thermal conductivity of a Ge QDs/SiO_2 system for clarifying the deviations between Ge QDs/SiO_2 system and the corresponding bulk materials. The dashed lines in Fig. 2(b) represent the $k(T)$ curves at the limit of the maximum thermal interface resistance for 4.9-, 6.3- and 7.6 nm-Ge QDs/SiO_2 samples, respectively, based on measured QD sizes and volume fractions from the corresponding TEM images. The effective media approach not only underestimates the magnitude decrement but also deviates the temperature dependence from experimental $k(T)$ data. Keeping the QD sizes unchanged in EMM, the best fit for measured $k(T)$ data is obtained by increasing volume fractions of 9.1, 5.3, and 15.9% for 4.9-, 6.3- and 7.6 nm-Ge QDs in oxide matrix to 15, 20, and 70%, respectively, in solid lines as shown in Fig. 2(b). Such enormously high volume fractions of Ge QDs together with ex-

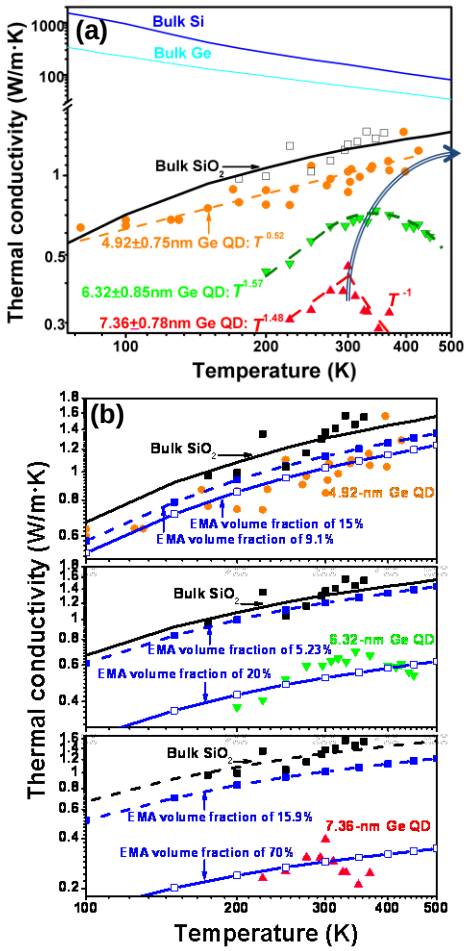

Fig. 2 (a) Temperature dependence of thermal conductivities for various-sized Ge QDs in SiO_2, bulk SiO_2, Si and Ge. (b) calculated thermal conductivities of Ge QDs/SiO_2 using effective medium approximation.

tremely large thermal interface resistances are not realistic in our studied samples. Significant discrepancies in magnitude and in temperature dependence of $k(T)$ between EMM simulation and experimental data suggest that in addition to enhanced boundary/surface scattering effects, some otherwise important mechanisms emerge to affect phonon transport in Ge QDs/SiO_2 system.

Thermal behaviors of Ge QDs/SiO_2 system appear to be considerably influenced by the QD size. For the 6.3 and 7.6 nm Ge QD, measured thermal conductivities initially follow a power law of $k(T) \propto T^{1.5}$ from 100 to around 300 K, deviating from the conventional Debye specific heat T^3 law for bulk crystal at low temperature, then reach their peak values around 345 and 298 K, respectively, which is in sharp contrast to the peak temperature of bulk Ge that occurs at about 25 K, and finally decreases with temperature, indicating the onset of Umklapp scattering that decreases the thermal conductivity because of anharmonic phonon-phonon interactions at high temperature. Whereas the thermal conductivity of the 4.9-nm-diameter QD increases mildly with temperature ($k(T) \propto T^{0.5}$) along with the absence of the Umklapp peak, probably originating from the fact of these QDs being much smaller than the phonon wavelength, which is in the range of 10-1000 nm for bulk Ge at 300 K, and consequently acting as effective defect scattering sites that lead to the characteristic $k(T)$ of the QD/SiO_2 system insensitive to temperature.

The inverse size-dependent Umklapp peak temperature suggests that throughout the experimental temperature range, phonon boundary scattering effects dominate for phonon transport within the Ge QD/SiO_2 system over unharmonic phonon–phonon scattering because the size of studied QDs is smaller than the phonon mean free path. However, the inverse dependence of magnitude and Umklapp peak on the QD size reveals that besides phonon boundary scattering, phonon confinement effects may emerge to play important roles, leading to modified phonon dispersion and lower averaged phonon group velocity, in particular at low temperature range (100-250 K). In addition, the acoustically mismatched barriers between the Ge QD and SiO_2 may also dramatically influence the phonon spectra, leading to a strong phonon depletion effect, where almost all the phonon modes are squeezed because of the redistribution of the elastic deformations in the acoustically mismatched QD. Such effects have also been observed in Ge/SiO_2 core-shell nanowire structures.

4. Conclusions

A significant reduction in magnitude together with a considerable deviation in temperature dependence from the corresponding bulk behaviors have been experimentally discovered from Ge/SiO_2 core-shell QDs when their diameter is less than 10 nm. Inverse size-dependent $k(T)$ and Umklapp peak temperature suggest that not only the phonon boundary scattering effects dominate for phonon transport in the Ge QD/SiO_2 system over the phonon–phonon scattering, but also phonon confinement effects emerge to modify the phonon dispersion, revealing the Ge QD/SiO_2 system a promising nanostructures for the incorporation with existing silicon TE structures.

Acknowledgements

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