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Microscopic phonon theory of Si/Ge nanocrystals

Abstract Microscopic phonon theory of semiconductor nanocrystals (NCs) is reviewed in this paper. Phonon modes of Si and Ge NCs with various sizes of up to 7 nm are investigated by valence force field theory. Phonon modes in spherical SiGe alloy NCs approximately 3.6 nm (containing 1147 atoms) in size have been investigated as a function of the Si concentration. Phonon density-of-states, quantum confinement effects, as well as Raman intensities are discussed.

Keywords semiconductor nanocrystal, alloy, phonon, lattice dynamics, Raman

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1 Introduction

SiGe has rich applications in high-speed inexpensive devices and has received plenty of interest in recent years [1]. Many optical, transport, and thermal properties of nanocrystals (NCs) are related to phonon properties [2–4]. Phonon properties of NCs are becoming more important. One kind of thermoelectric material is Si and Ge NCs [5–7]. The increase in the figure of merit is mainly related to the minimization of thermal conductivity of phonons [6, 7]. Currently, most of the theoretical understanding of phonon modes in NCs is based on continuum dielectric models [8–10]. However, one of the basic assumptions of all dielectric models is that the material is homogeneous and isotropic, i.e., only valid in the long wavelength limit. When the size of NCs is small, in the range of a few nm, the continuum dielectric models are intrinsically limited. In recent years, we have developed a microscopic valence force field model (VFFM) [11] to study phonon modes in NCs [7, 12–19].

Raman spectroscopy is a powerful tool to detect phonon properties in Si/Ge NCs. Quantum confinement effects as well as matrix effects can be detected in Raman spectra. Raman spectra of ultra-thin Ge film grown on Si [100] surface [20], Ge/Si superlattice [21], and self-organized Ge quantum dots superlattice grown on Si substrates [22] have been reported. Raman spectra of Si, Ge, and SiGe alloy NCs can be calculated by bond-charge approximation [12, 23]. In this paper, we review briefly some of the phonon-related properties of Si, Ge and SiGe alloy NCs in microscopic phonon theory. The calculated spectra are compared with available experiments.

2 Valence force field model (VFFM)

The microscopic VFFM used in calculations of NC phonons has been described in detail in publications [11, 12]. The potential energy difference ΔE in the VFFM for bond stretching and bond angle bending is

$$\Delta E = \sum_i C_0(\Delta b_i/b)^2/2 + \sum_j C_1(\Delta \theta_j)^2/2$$

where the two force constants are chosen to be $C_0 = 49.1$ eV, $C_1 = 1.07$ eV for Si, and $C_0 = 47.2$ eV, $C_1 = 0.845$ eV for Ge [11]. The first summation is over all the bonds $i$ of equilibrium length $b$, while the second summation is over all the bond angles $j$. In the alloys, there are Si-Si, Si-Ge, and Ge-Ge bonds. The force constants
of all bonds are assumed to be the same as Ge. The Si and Ge masses are taken as 28.09 and 72.59 atomic units, respectively. The highest Si bulk optical phonon frequency calculated in this mass-difference approximation is 502 cm\(^{-1}\), which differs from the experimental value of 520 cm\(^{-1}\) by only 3%. This suggests that the mass-approximation used in the calculations is reasonably good. From Eq. (1), the dynamical matrix can be constructed for a Si/Ge NC. The assumption that the Si/Ge NC is symmetrical enables the use of group theory to reduce the dimension of the dynamical matrix. By solving the dynamical matrix, the frequencies as well as eigenvectors of phonon modes are obtained.

3 Phonon density of states of Ge NCs

The Ge NCs in our calculations are spherical and of \(T_d\) symmetry. The spherical NCs are constructed in the following manner: The smallest NC has five atoms, with one inner atom surrounded by four nearest atoms. The next larger NC has 17 atoms, with each of the four outer atoms surrounded by another three atoms. Other larger NCs are constructed by adding spherical layers of atoms one by one in the same manner. The highest possible point group \(T_d\) symmetry of these Ge NCs allows us to calculate phonons of NCs with diameter of up to 7 nm (8105 Atoms). In our investigations, we calculated phonon modes in Ge NCs with two different types of surfaces (free standing surface and fixed surface) in the size range from five atoms up to about 7 nm in diameter [13]. Realistic NCs are usually embedded in a matrix with boundary conditions between the above two surfaces. The phonon density of states [PDOS \(D(\omega)\)] of Ge NCs with the two types of surfaces and a few sizes are shown in Fig. 1. The left panel is for Ge NCs with a fixed surface, while the right panel is for Ge NCs with a free surface. Comparing these results, it is observed that there are more low frequency peaks in Ge NCs with a free surface than in Ge NCs with a fixed surface. As the size of the Ge NCs increases, the frequency of the highest optical modes is blue-shifted. This is indicative of the quantum confinement effect as discussed in Ref. [12]. This is particularly obvious when the nanocrystal diameter is less than 3 nm. When the size of Ge NCs increases up to 7 nm, the PDOS of Ge NCs with these two different surfaces both approach that of the bulk. One major feature of phonons in Ge NCs with a fixed surface is that there is always a major peak at the frequency of about 211 cm\(^{-1}\), which corresponds to the frequency range between the optical and acoustic phonons of the bulk Ge. This peak represents interface phonons, which are still strong in Ge NCs of 7 nm, or the maximum size of our present calculations.

![Fig. 1](image)

4 Phonon density of states of Si\(_x\)Ge\(_{1-x}\)NCs

Phonon modes of Si NCs follow similar rules as Ge NCs discussed above [12, 13]. The PDOS of spherical Si\(_x\)Ge\(_{1-x}\) alloy NCs containing a total of 1147 atoms (diameter \(d \sim 3.7\) nm for pure Ge and \(d \sim 3.5\) nm for pure Si) with varying fractions of Si is shown in Fig. 2. In our calculations, we assume that the Si atoms are randomly distributed within the NC, and there is no ordering of any type in the NCs. In particular, there is no long-range ordering of the Si and Ge atoms which has been found experimentally to give rise to well-defined Raman peaks of around 255 and 435 cm\(^{-1}\) [24]. The force constant parameters of the Si\(_x\)Ge\(_{1-x}\) are chosen the same way as the Ge parameters [15]. Since Si and Ge bulk materials have different lattice constants, the lattice constant of the alloy Si\(_x\)Ge\(_{1-x}\) is approximated by an interpolation between those of Si and Ge using Vegard’s law [25], 
\[
a = xa_\text{Si} + (1-x)a_\text{Ge},
\]
where \(a_\text{Si}\) and \(a_\text{Ge}\) are the lattice constants of Si and Ge respectively, and \(x\) is the silicon fractional concentration. We typically start from a small NC that is approximately spherical in shape.