Size and temperature dependence of the energy gaps in Si, SiC and C quantum dots based on tight-binding molecular dynamics simulations

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Abstract

We investigated the size and temperature dependence of the energy gaps in H-terminated Si, SiC, and C quantum dots with diameters ranging from 1 to 10 nm, using tight-binding molecular dynamics (MDs) simulations. For the quantum dots with more than 1000 atoms, the order-N Krylov subspace method was employed. From our results, we formulated the energy gaps of the quantum dots as a function of their size and temperature. Our formula is applicable to the estimation of the energy gaps at any given temperature in the 0–600 K range, for a wide variety of quantum dot sizes (from a small quantum dot to bulk). The calculated energy gaps were in good agreement with the experimentally measured values. The thermal fluctuations of the band gap for a Si quantum dot were also analyzed in detail. We found that, unlike the case of bulk, the decrease in the energy gap at higher temperatures is predominantly caused by an increase in the splitting of the HOMO levels, with only a small contribution from the size expansion effect. For the temperature dependence of the energy gap of Si quantum dots, we also examined the effect of the media surrounding the quantum dots by performing tight-binding MDs simulations at finite temperatures with and without the restriction on the freedom of the motion of the surface H atoms. Our results have clarified that the temperature dependence of the energy gaps of quantum dots in a medium with weak restrictions on the freedom of the surface atomic motion (e.g., in gas or liquid) is larger than in a medium with strong restrictions (e.g., like SiO₂), especially in the case of small quantum dots.

1. Introduction

Various kinds of nano-structured materials such as quantum dots, in which novel physical and chemical properties appear by the miniaturization of the bulk materials, have been studied to realize desirable and tunable properties suitable for various applications. Since Silicon is a resource in abundant supply with high safety to the environment and the human body, Si quantum dots particularly attract much attention as one of the promising candidates of materials for the applications to solar cell, alternatives to traditional organic dyes, photo-sensors, light-emitting diodes, single electron devices, bio-medical tags, and so on [1–8]. Although the investigations on C and SiC quantum dots [9–11], which consist or include another abundant resource in group IV element, C, are not as extensive as those on the Si quantum dots, an understanding of the behavior of energy gaps of these systems in wider ranges of temperature and size will open up newer avenues for applications.

One of the major challenges is to obtain desirable energy gaps of quantum dots suitable for each device by tuning the size, structure, composition, and so on, especially in optical and electronic applications. Si quantum dots for optical applications have been made using several epitaxial methods, and the energy gaps have been analyzed. According to photoluminescence (PL) experiments, the peak energies of PL spectra corresponding to the energy gaps increase as the quantum dot size decreases [12–17]. This is explained with the effective mass...
theory, using a semi-classical or semi-quantum approach, in which the peak energies of PL vary as \(1/D^2\) with the diameter \(D\) of the quantum dot. These phenomena originate from the quantum confinement effects of electrons and holes inside the dots.

The relationship between the energy gaps and the diameters of the ideally spherical Si quantum dots has also been investigated by first-principles calculations [18–23]. Chelikowsky et al have investigated the electronic structures of the Si dots based on the real space band structure method using the density functional theory (DFT) within the local density approximation (LDA) [18]. They have examined dots in the range of 0.3 (1 Si atom) to 7.0 (9041 Si atoms) nm in diameter, and found that the energy gaps of the dots decrease as the diameters increase, and that the ionization potentials and electron affinities of the dots over 5 nm in diameters are almost the same as those of the Si bulk crystal. Iwata et al have investigated the density of states of Si quantum dots of larger sizes using the real space band structure method within DFT-LDA [19, 20]. They have performed the calculations for dots ranging from 2.3 (318 Si atoms) to 7.4 (10701 Si atoms) nm in diameter on massively parallel computers. They observed that the density of states of dots with diameter more than 6 nm (6000 Si atoms) is almost the same as that of the Si bulk crystal. For quantum dots of a smaller size, in which the exciton effect cannot be negligible, higher accuracy methods such as the time-dependent DFT or multi-reference second-order perturbation theory are required to compare the calculated electronic structures with experimental ones [21, 22]. Using such high accuracy calculations, Garoufalis et al have calculated the optical gap of Si quantum dots and found that the Si dots smaller than 2.2 nm in diameters could emit visible light [21]. Molteni et al have investigated pressure-induced structural transformations in small silicon clusters containing less than about 70 Si atoms with first-principles molecular dynamics (MD) method and calculated the time evolution of the Kohn–Sham energy gap of Si\(_{13}\)H\(_{16}\) cluster under pressure [23]. While these theories have a high accuracy, they come with a high computational cost.

For industrial applications, the optical and electronic properties require to be controlled as precisely as possible in order to achieve excellent performance. Thus, it is essential to know the dependence of the energy gaps of quantum dots, not only on the size but also on the temperature accurately. Numerous experiments show that the energy gaps of Si quantum dots decrease as temperature increases [24–28]. Such temperature dependence is very similar to that occurring in crystals, usually attributed to the thermal lattice expansion and electron–phonon interactions [29–33]. From an atomistic point of view, on the other hand, little is known about the mechanism behind the temperature dependence of the energy gaps of quantum dots. It is, therefore, important to elucidate this mechanism, taking into account the structural fluctuation that is supposed to become larger due to miniaturization. Few electronic structure calculations, however, have been performed on the temperature dependence of energy gaps and the thermal fluctuation of the gaps, because of the large computational costs involved, especially when first-principles methods are employed.

The tight binding (TB) method is one of the most effective ways to reduce computational costs [2, 34–40]. Wolkin et al [2], Niquet et al [38], and Ren et al [39] have investigated the energy gaps of Si quantum dots using TB methods. Their results well reproduce the energy gaps of Si quantum dots obtained from time dependent density functional calculations [21] as well as the calculations employing empirical pseudopotentials and the configuration interaction method [41]. In their calculations, however, the structural relaxation is neglected and the TB parameters independent of the atomic distances are employed. The TB–MD calculations of the pressure-induced structural transformations in a Si nanocrystal have also been reported [40]. In this investigation, however, the calculations have been done for Si clusters containing less than about 700 atoms and the temperature dependence of the energy gap has not been discussed.

In this paper, we employ the TB scheme with atomic–distance-dependent parameters to describe the dynamical behavior of atoms at finite temperatures. As the computational cost of TB calculations is much lower than that of the first-principles calculations, we can perform geometry optimizations, temperature-controlled MD, and the analysis of the fluctuations of band gaps of quantum dots containing more than 1000 Si atoms at several finite temperatures with reasonable costs.

In the following, we explain the detailed calculation methods and models in section 2. In section 3, we analyze and discuss the size and the temperature dependence of the energy gaps for Si, 3C–SiC, and C quantum dots. We also propose analytic expressions for the energy gap, \(E_g(D, T)\), as a function of both diameter \(D\) and temperature \(T\) of the quantum dots, where the parameters of these analytic functions are fitted to our results of the TB calculations at finite temperatures. Finally, we summarize our results in section 4.

2. Methodology

2.1. TB scheme and models of semiconductor quantum dots for MD simulations
It is well known that TB calculations of the Si crystal using only its s and p orbitals do not yield the conduction band minimum at the correct k-point between the \(\Gamma\) and X points. On the other hand, the \(sp^3\) TB calculations,
which are similar to the Goodwin, Skinner, and Pettifor model in crystals. In order to simulate hydrogenated quantum dots, we introduced a different form of the pairwise potential for Si and the binding energies of SiH4 and CH4 obtained by previous TB calculations.

4 To investigate the electronic properties of the quantum dots at finite temperatures, we need the TB parameters for the Si–H and C–H pairs at the surface of the quantum dots. The parameters for Si–H and C–H proposed by Ivashchenko et al. [49], however, are optimized for those in crystals. In order to simulate hydrogenated quantum dots, we introduced a different form of the pairwise potential for Si–H and C–H which are similar to the Goodwin, Skinner, and Pettifor model [50], and newly determined the parameters to reproduce the bond lengths and the binding energies of SiH4 and CH4 obtained by previous TB calculations [51, 52].

Table 1. Calculated lattice constants (a0), bulk moduli (B), energy gaps (Eg), and widths of valence bands (W). Experimental values are also shown. The band structures are shown in figure B1 in appendix B.

|         | This work | Experiment |
|---------|-----------|------------|
| Si      | a0 (Å)    | 5.41       | 5.43 [53] |
|         | B (GPa)   | 126        | 102 [54]  |
|         | Eg (eV)   | 1.17       | 1.17 [30]  |
|         | W (eV)    | 11.9       | 12.4 [55] |
| 3C–SiC  | a0 (Å)    | 4.37       | 4.36 [56]  |
|         | B (GPa)   | 272        | 224 [57]  |
|         | Eg (eV)   | 2.40       | 2.416 [58]|
|         | W (eV)    | 16.0       | —          |
| C       | a0 (Å)    | 3.61       | 3.57 [59]  |
|         | B (GPa)   | 463        | 442 [60]  |
|         | Eg (eV)   | 5.50       | 5.49 [61]  |
|         | W (eV)    | 21.5       | 21 [62]   |

in which the excited state of the s orbital is taken into account, give the correct position of the conduction band minimum, and the HOMO-LUMO gap of Si quantum dots almost reproduce the results of the first-principles calculations [42–44]. It has also been reported that the situation is the same in the case of C [42, 45, 46].

Thus, to investigate the electronic properties of semiconductor quantum dots, we employed the sp3’s* TB scheme. The atomic–distance-dependent TB parameters proposed by Ivashchenko et al. were used for the Si–Si, Si–C, and C–C [47, 48]. The form of the pairwise potential and the parameters relating to the Si–H and C–H pairs were newly determined for our TB–MD simulations based on the previous studies [49–52]4. Details of our TB–MD method are described in appendix A.

Prior to investigating the electronic states of quantum dots, we briefly examined the Ivashchenko’s TB parameters by calculating the optimum lattice constants, bulk moduli and band structures of crystal Si, 3C–SiC, and C. We used the primitive unit cell including 2 atoms under the periodic boundary condition, 10 × 10 × 10 k-points in the Brillouin zone, and the ordinary matrix diagonalization scheme. The results well described the experimental values as shown in table 1 and the positions of the conduction band minima in band dispersions (E–k curve) of crystal Si, SiC and C (figure B1 in appendix B).

In order to investigate the band gap dependence on the size of quantum dots, we modeled them as spherical clusters. At the bare surface of the clusters, there exist at most two dangling bonds of the host atoms. We terminated them by H atoms. Then, we relaxed the initial structure of each nano-sized semiconductor cluster including the H atoms. In all the calculations, we have employed the super cell model. Each cluster is placed in a cubic unit cell whose length of a side (a) is large enough to separate the clusters in the neighboring cells (a ≳ D + 7 Å). Under this condition, the distances between any cluster surfaces are larger than the TB cutoff distance. Thus, we prepared eight Si, seven 3C–SiC, and seven C spherical clusters of various size, as listed in table 2. All of the eight Si clusters are shown in figure 1.

The steepest descent method was used for geometry optimization, in which, the tolerance for the forces acting on atoms is 5.1 × 10−2 eV Å−1. The MD simulations were performed for the NVT ensembles at T = 200, 400, and 600 K. The velocity Verlet algorithm was used for the time evolution of atomic positions and velocities with a time step of 1 fs. Electronic structures were investigated for all of the quantum dots, and the energy gaps at finite temperatures were also evaluated for all dots, excepting the largest Si one and the first and second largest ones for 3C–SiC and C. For these large semiconductor dots, we evaluated the energy gap (Eg) at 0 K using the Krylov subspace method explained in the next subsection. Only the Γ-point was sampled in the Brillouin zone throughout the electronic structure calculations for geometry optimizations and MD simulations.

2.2. Order(N) algorithm based on the Krylov subspace method

In the electronic states calculations of the quantum dots consisting of less than 1000 atoms, we evaluated the eigenvectors and eigenvalues of the TB Hamiltonian using the ordinary matrix diagonalization method. In these
3. Results and discussions

3.1. Energy gaps of Si-, SiC- and C-quantum dots at 0 K

The densities of states (DOS’s) of the Si quantum dots, constructed using the calculated eigenvalues, change drastically from discrete to continuous in the range of quantum dot sizes studied here (1.1–5.8 nm in diameter). We have displayed four DOS’s in figure 2. The smaller Si quantum dots (a) 1.1 and (b) 2.2 nm in diameter have discrete DOS’s and large energy gaps (3.66 eV and 2.09 eV, respectively). The DOS’s of the 5.8 and 10.2 nm Si quantum dots in figures 2(c) and (d) appear very similar to that of bulk Si, except for peaks appearing around −7.5 eV, which originate from the surface Si–H bonding states. These dots have continuous DOS’s and smaller energy gaps (1.34 eV and 1.22 eV, respectively).

In figure 3, we plot the energy gaps between the highest occupied and the lowest unoccupied states for 8 Si quantum dots, $E_e$ for bulk Si is also plotted. We overlay the $E_e$–$D$ curve for $D < 5$ nm that was obtained using the TB method by Wolkin et al only for small Si quantum dots [2] on our plots. Our results agree well with theirs in the smaller cluster size range ($D < 5$ nm), and smoothly approach the energy gap of bulk Si, 1.17 eV, as D increases, covering the wide range from small quantum dots to bulk Si. (We should note that a few papers on the calculation of Si quantum dots [21, 41] use the Wolkin’s results as experimental values. Authors of these papers argue that correspondences between their calculated values and Wolkin’s experimental values are evidence of the validity of their calculations, although the referred Wolkin’s values are not experimental ones but the TB calculation results. Wolkin et al did not mention the experimental values of the quantum dot sizes directly, but plotted their measured optical gaps on the $E_e$–$D$ curve obtained using the TB method, for the purpose of estimating the Si dot sizes from their curve.)

Here, we fit a curve to the calculated energy gaps of Si quantum dots with the function

$$E(D) = E_0 + \frac{A}{D^2},$$

(1)

where $E(D)$ is the energy gap at size $D$, $E_0$ is the energy gap at $D = 0$, and $A$ is a constant.

Table 2. Model quantum dots of Si, 3C–SiC, and C and their diameters. X is C or Si.

| Model cluster | Diameter (nm) |
|---------------|--------------|
| Si            | 3C–SiC       | C           |
| X55H56        | 1.1          | 0.9         | 0.7        |
| X27H26        | 1.5          | 1.2         | 1.0        |
| X211H72       | 2.2          | 1.8         | 1.3        |
| X53H32        | 2.7          | 2.2         | 1.8        |
| X108H112      | 3.5          | 2.8         | 2.3        |
| X516H1182     | 5.8          | 4.7         | 3.8        |
| X10110H1864   | 7.2          | 5.9         | 4.8        |
| X51111H3708   | 10.2         | —           | —          |

Note. The diameters of quantum dots ($D$) were determined by $D = 2(3N/4\pi\rho)$, where $N$ and $\rho$ are the number of host atoms and the density of each crystal obtained from our calculations on crystals.
which expresses an energy eigenvalue for an electron confined in a spherical quantum well with diameter $D$ and an infinite barrier height \cite{65–67}. $E_0$ is the band gap of bulk Si, 1.17 eV. The dashed line in figure 3 is the optimized plot of the function (1) using the least squares fitting method. In the fitting procedure, we excluded the values of the two smallest quantum dots from a series of target values and set size-dependent weights for the fitting\footnote{We set the weights for fitting method as follows. In Si clusters, the weights are 0.1 for $D = 1.5$ nm, 0.4 for $D = 2.2$ nm, and 1.0 for the others. In SiC clusters, the weights are 0.1 for $D = 1.2$ nm, 0.4 for $D = 1.8$ nm, and 1.0 for the others. In C clusters, the weights are 0.1 for $D = 1.0$ nm, 0.4 for $D = 1.5$ nm, and 1.0 for the others.}, because any trials containing the values of the smallest quantum dots while giving same weights for all quantum dots in the fitting procedure have enlarged differences for the medium sized (2.2, 2.7, and 3.5 nm diameter) quantum dots.

Figure 1. Models of Si quantum dots. The surface dangling bonds of the Si clusters are terminated by H atoms. (a) Si quantum dots with diameters ranging from 1.1 to 10.2 nm. (b) The perspective view of the 2.2 and 2.7 nm Si quantum dots.
We also attempt to fit our results with an extended function

\[ E(D) = E_0 + \frac{a'}{D^2} + \frac{b'}{D}, \]  

which adds another term \( b'/D \) to equation (1), mainly to correct the deviation of the form of the potential well from the ideally spherical one with an infinite barrier height. The solid line in figure 3 is the optimized plot of this function, also using the least squares fitting method, where we excluded the smallest quantum dot of 1.1 nm diameter from a series of target values and assigned the weights depending on the sizes (see footnote 5), similar to the fitting procedure followed for function (1). Function (2) improves the agreement, in particular for the second smallest dot. The curves in figure 3 show that both functions fit our calculation values well over a wide range; even the function (1) fits over a wider range (from 2.2 nm to bulk) than the applicable range (\( \sim 20 \) nm) predicted by the effective mass theory, whose range was proposed by Kayanuma [67] for the energy gaps of Si quantum dots. The optimized values of the parameters in equations (1) and (2) are shown in table 3.

Figure 4 shows the energy gaps calculated using the TB method for 3C–SiC and C quantum dots. The energy gap of the smallest 3C–SiC (C) quantum dot of \( D = 0.8 \) (0.7) nm is 5.54 (9.63) eV. The energy gap decreases as the dot size increases and for the largest dot of \( D = 5.8 \) (4.8) nm it reaches 2.51 (5.71) eV, which is close to the
band gap of bulk 3C–SiC (2.40 (5.50) eV). We fitted curves to these energy gap values with equations (1) and (2) using the least squares fitting method, as applied for the Si quantum dots. The weight factors of the 3C–SiC and C quantum dots are the same as those in the case of the Si quantum dots (see footnote 5). Both equations (1) and (2) reproduce the energy gaps well over wide ranges; also in this case, equation (2) improves the applicable range (from 1.2 nm for 3C–SiC and 1.0 nm for C, respectively, to the bulk (crystal)).

3.2. Energy gaps of quantum dots at finite temperatures

Next, we examine the size and temperature dependence of the energy gaps of Si, SiC and C quantum dots. Finite temperature MD simulations at 200, 400, and 600 K have been performed for these dots excluding the smallest ones, which were difficult to be described even in the static calculations with equations (1) and (2) and the larger ones due to the heavy computational costs: thus, the simulated quantum dots are six—from Si$_{87}$H$_{76}$ to Si$_{1011}$H$_{1864}$ for the Si, and four from X$_{86}$H$_{76}$ to X$_{1087}$H$_{412}$ for the SiC and C cases. Each of the initial structures of the dot at 200, 400, and 600 K was prepared by expanding the corresponding dot which was structurally optimized at 0 K, according to the thermal expansion coefficient ($2.59 \times 10^{-6}$ K$^{-1}$ [53] for Si, 2.77 Si$^{-6}$ K$^{-1}$ [68] for 3C–SiC and 1.05 Si$^{-6}$ K$^{-1}$ [68] for C). After each system reached equilibrium in a 1 ps MD simulation, we performed another 10 ps MD simulation, and evaluated the energy gaps by averaging over all the MD steps in the 10 ps. During the simulations, only the positions of the surface H atoms of the quantum dots were fixed to represent the restriction by the surrounding materials, like SiO$_2$. (The effects of the relaxation of surface H atoms will be discussed later in this section.) For the larger dots ($X_n H_m, n \geq 1087$), we sampled randomly 100 of the 10 000 configurations generated during the 10 ps MD simulation and calculated energy gaps to evaluate the average, because of the heavier computational cost involved, even using the efficient shifted COCG method. The energy gaps obtained from our simulations are plotted in figure 5. With increase in dot size, the differences between the energy gaps at different temperatures become smaller. In the case of Si quantum dots, the differences between the energy gap at 0 K and 600 K are 0.27 eV, 0.23 eV and 0.14 eV for dots with $D = 1.5$ nm, 2.2 nm and 7.2 nm, respectively. In the case of SiC (C) quantum dots, they are 0.49 (0.47) eV and 0.38 (0.30) eV for the dots with $D = 1.2$ (1.0) nm and 2.8 (2.3) nm, respectively.

Here, we formulate the size and temperature dependence of the energy gaps with the addition of a temperature dependent term in equation (2), constructed so as to reproduce the temperature dependence of the energy gaps of bulk systems [29], as follows:

$$E_g(D, T) = E_0 + \frac{a}{D^2} + \frac{b'}{D} - \left( c + \frac{d}{D^2} \right) \left( \frac{T^2}{T + e} \right).$$
The determined values of except for those of X86H76, are in good agreement with value of obtained through the least squares (quantum dot sizes is about 1 nm at any temperature through 0°C quantum dots, respectively. Equation where and 0.12 eV for the Si, SiC, and C quantum dots, respectively. The diameters considered are 2.5, 3.0, 3.5, 4.0 and 4.5 nm and temperature rises, more the energy gaps decrease. For example, the energy gap for the Si quantum dot with determined by the difference between the LUMO and HOMO levels. Figure 7 where the curves clearly. The size and temperature dependences of the energy gaps of quantum dots of finite temperatures. Figure 7, we plot the temperature dependence of the energy gaps given by equation the curves of equation denote calculated values for 0, 200, 400, and 600 K, respectively. The solid, dashed, dotted, and dashed–dotted lines are the best fitting curves of equation (3) to the given sets of data. (Note that the values of diameter are plotted logarithmically to show the difference of the curves clearly.)

Table 4. Optimized values of c and d in equation (3). The values of e are the experimental ones.

|      | c (eV K⁻¹) | d (eV nm² K⁻¹) | e (K)  |
|------|------------|----------------|--------|
| Si   | H fixed    | 5.83 × 10⁻⁴    | 1.41 × 10⁻³ | 636 [69] |
|      | H free     | 5.19 × 10⁻⁴    | 3.39 × 10⁻³ | 636 [69] |
| 3C–SiC | H fixed   | 1.20 × 10⁻³    | 3.75 × 10⁻³ | 1200 [70] |
| C    | H fixed    | -4.08 × 10⁻⁴   | -1.38 × 10⁻³ | -1437 [46] |

where and are set to the values (table 3) determined at 0 K for the equation (2). The terms , and were obtained through the least squares fitting procedure. Equation (3) is rather insensitive to the variations in the value of around the value proposed for the bulk. Hence, we choose the proposed bulk values [46, 69, 70] for c. The determined values of , and are listed in table 4. The calculated energy gaps of D–diameter dots at T(K), except for those of X86H76, are in agreement with of equation (3) within deviations of 0.05, 0.06, and 0.12 eV for the Si, SiC, and C quantum dots, respectively. of the smallest quantum dots X86H76 show larger deviations from the calculated energy gaps: the differences are 0.17, 0.16 and 0.50 eV for Si, SiC, and C quantum dots, respectively. Equation (3) with the given parameters are applicable to estimate the energy gaps at any temperature through 0–600 K, for vast ranges of dot size.

In figure 6, we plot the temperature dependence of the energy gaps given by equation (3) with the optimized parameters, for several sizes of Si quantum dots. The diameters considered are 2.5, 3.0, 3.5, 4.0 and 4.5 nm and the range of temperatures is 0–600 K. At low temperatures, the energy gaps decrease slowly. The higher the temperature rises, more the energy gaps decrease. For example, the energy gap for the Si quantum dot with reduces by about 0.01 eV in the range of 0–100 K, while it decreases by 0.043 eV in the range of 300–400 K. Experimental values for the dot with D = 4.1 nm [24], which are plotted in figure 6, are well reproduced by when D = 4.0 nm. Here we remark that the experimental measurement error of quantum dot sizes is about 1 nm [71]; hence the difference of 0.1 nm between the experiment and our calculation falls within this error.

Here, we examine the thermal fluctuations in the energy gap of the Si quantum dot with D = 2.2 nm (Si281H172) at finite temperatures. Figure 7(a) shows the fluctuations in the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) at 600 K. The three-fold degenerate HOMO level at 0 K splits and the energies fluctuate with time. The amplitude of the thermal fluctuations of the HOMO levels is larger than that of the LUMO levels. The energy gap at an MD time step is determined by the difference between the LUMO and HOMO levels. Figure 7(b) shows the time-fluctuation and the population of the energy gap in the 0.0–10.0 ps timescale at 0, 200, 400 and 600 K. Population of the energy gap becomes broad and the averaged energy gap (the center value of the population) becomes smaller with increase of temperature. The decrease of the energy gap is caused by increase of splitting of the HOMO levels with the increase in temperature. As can be deduced from equations (1) and (2), size expansion effect gives only a
small contribution to the decrease in the energy gap unlike in the case of bulk, because the diameter of the quantum dot at 600 K is only 100.49% as that at 0 K.

In order to describe quantum dots in an environment such as a liquid solution or on surfaces of materials [9–11], we have performed finite temperature MD simulations again while relaxing the surface H atoms for the Si quantum dots with $D = 2.2, 2.7, 3.5, 5.8,$ and $7.3$ nm. Figure 8 shows the temperature dependence of the energy gaps for the Si quantum dots with relaxed and fixed H atoms. The graph of figure 8 indicates that the effect of the constraint of the surface-terminating H motion becomes smaller as the dot size increases.

Figure 6. The temperature dependence of the energy gap of Si quantum dots. The curves are calculated using equation (3) for the dots 2.5, 3.0, 3.5, 4.0, 4.5 nm in diameter. The open squares show the experimental values for the dots of diameter 4.1 nm embedded in SiO$_2$.

Figure 7. Thermal fluctuations of energy levels and energy gaps. (a) HOMO and LUMO energy levels of the Si quantum dot with a diameter of 2.2 nm at 600 K. (b) Thermal fluctuations and populations of the energy gap for the 2.2 nm Si cluster at 0, 200, 400, and 600 K. The energy gap is defined by the difference between the HOMO and LUMO energy levels, at every MD time step.

The graph of figure 8 indicates that the effect of the constraint of the surface-terminating H motion becomes smaller as the dot size increases.
In Figure 9, we plot the energy gaps at 300 and 600 K using equation (3) with the optimized parameters listed in tables 3 and 4, for Si, 3C–SiC and C quantum dots with fixed surface H atoms. The energy gaps predicted by equation (3) distribute over vast ranges: \( \sim 2.83 - 1.11 \) (\( \sim 2.59 - 1.00 \)) eV for the Si dots, \( \sim 4.10 - 2.33 \) (\( \sim 3.57 - 2.16 \)) eV for the SiC dots and \( \sim 8.61 - 5.47 \) (\( \sim 7.98 - 5.32 \)) eV for the C (SiC) at 300 K (600 K). Colors of light corresponding to the energy gaps are indicated in the bar on the right. The ranges for the Si and SiC quantum dots contain energy gaps of visible light, indicating their applicability as photovoltaic materials. Equation (3) is also a functional tool to design quantum dot devices with desired properties. Quantum dots embedded in media like SiO\(_2\) were simulated using the simple models while fixing H atoms. Watanabe et al\cite{72} investigated the electronic structure of Si dots surrounded by SiO\(_2\) within the scope of static calculations. Further TB parameter development for an Si–O system performed so as to reproduce the bonding character at the interface between the embedded SiO\(_2\) and the Si dots, such as in [72] would enhance the prediction accuracy of the size and temperature dependence of the energy gaps through dynamical simulations on the whole SiO\(_2\)–Si system, similar to that explained in this paper.

4. Summary

In this study, we have investigated the size and temperature dependence of the energy gaps of Si, SiC, and C quantum dots containing from 35 to 28111 host atoms, using the tight-binding MDs method. For the quantum dots consisting
of more than 1000 atoms, we used the order-N Krylov subspace method. Temperature-controlled MDs simulations were performed for the quantum dots consisting of less than about 10,000 atoms, and static calculations were done on those consisting more than 10,000 atoms. From the results of our simulations, we found that the temperature dependence of the energy gap becomes larger when the size of quantum dot reduces. We formulated the energy gap of the quantum dot as a function of the diameter and temperature. To investigate the origin of the temperature dependence of the energy gap, the thermal fluctuations of the energy gap were analyzed in detail on a Si quantum dot. We found that, unlike the case of bulk, the decrease in the energy gap at higher temperatures is mainly caused by an increase in the splitting of the HOMO levels, with only a small contribution from the thermal expansion effect. For the temperature dependence of the energy gap of Si quantum dots, we also examined the effect of media surrounding the quantum dots by fixing or relaxing the surface H atoms. We have shown that the temperature dependence of the energy gaps of quantum dots in a medium with weak restrictions on the freedom of the atomic motion near the surface, like a gas or liquid, is larger than in a medium with strong restrictions like SiO₂, especially in the case of small quantum dots. Our formula (equation (3)) is applicable to estimate the energy gaps at any temperature between 0 and 600 K, for a vast range of sizes ranging from small quantum dots to bulk, and well reproduce the experimental results. This will be especially useful to design photovoltaic materials, quantum dot devices, and so on with highly desired properties.

Appendix A

In the TB method, the total energy of a system is described as follows: [35, 36]

\[
E_{\text{tot}} = \sum_{i} \frac{p_i^2}{2m_{i}} + \int d\mathbf{k} \sum_{n} \langle \varphi_{n,k} | H_{\text{TB}} | \varphi_{n,k} \rangle f(\varepsilon_{n,k}) + E_{\text{rep}},
\]

(A1)

where the first, second and third terms are the kinetic energy of atoms, the electronic energy, and the ion–ion repulsive potential including the correction for double counting of electron–electron interactions of the second term, respectively. We denote \(p_i\), \(m_i\), \(H_{\text{TB}}\), \(\varepsilon_{n,k}\) and \(\varphi_{n,k}\) as the momentum, mass of the \(i\)th atom, TB Hamiltonian, Fermi–Dirac distribution function, eigen value and wave function of the \(n\)th eigen state for wavevector \(\mathbf{k}\), respectively. The wave function \(\varphi_{n,k}\) is expanded by local atomic orbitals as

\[
\varphi_{n,k} = \sum_{A,i,\alpha} c_{A,i,\alpha,k} \phi_{A,i,\alpha}.
\]

(A2)

Here, suffixes \(A\), \(i\), and \(\alpha\) denote the atomic species, atom’s sites, and atomic orbitals (i.e. \(s\), \(p_x\), \(p_y\), \(p_z\) for the \(sp^3\)–TB scheme) and \(\phi_{A,i,\alpha}\) is the local atomic orbital. In order to evaluate the coefficients of the local atomic orbitals \(c_{A,i,\alpha,k}\), we solved the eigen problem described as follows:

\[
\sum_{A,i,\alpha} \langle \phi_{B,j,\beta} | H_{\text{TB}} | \phi_{A,i,\alpha} \rangle c_{A,i,\alpha,k} = \varepsilon_{n,k} \sum_{A,i,\alpha} \langle \phi_{B,j,\beta} | \phi_{A,i,\alpha} \rangle c_{A,i,\alpha,k}.
\]

(A3)

In the TB model proposed by Ivashchenko et al. [47, 48] the matrix elements of \(H_{\text{TB}}\) are expressed using the atomic–distance–dependent forms, and the overlap integrals of wave functions are approximated by delta functions, \(\langle \phi_{B,j,\beta} | \phi_{A,i,\alpha} \rangle \approx \delta_{\alpha_A,\beta_B} \delta_{i_A,j_B} \delta_{\alpha_{A,i},\beta_{A,j}}\).

For the relaxation of the structures and the MD simulations at finite-temperature, we evaluated the force acting on each atomic site:

\[
F_i = -\int d\mathbf{r} \frac{d}{dr} \left\{ \sum_n \langle \varphi_{n,k} | H_{\text{TB}} | \varphi_{n,k} \rangle f(\varepsilon_{n,k}) \right\} - \frac{dE_{\text{rep}}}{dr}.
\]

(A4)

According to Hellmann–Feynman theorem, the first term of the right side of equation (A4) is written as

\[
-\int d\mathbf{k} \sum_n f(\varepsilon_{n,k}) \sum_{A,i,\alpha,B,j,\beta} c_{A,i,\alpha,k}^* \frac{d}{dr} \langle \phi_{B,j,\beta} | H_{\text{TB}} | \phi_{A,i,\alpha} \rangle c_{A,i,\alpha,k}.
\]

(A5)
Appendix B

Figure B1. Band structures for (a) Si, (b) 3C-SiC, and (c) C crystals and the density of state (DOS) for Si with parameters of Ivashchenko et al [47, 48] using sp$^3s^* \text{ orbitals. We show 8 bands of the the lower energies. The origin of the energy is set at the valence band top in each case. For Si and C, the sp}^3s^* \text{ TB calculations give the conduction band minimum at the correct } \mathbf{k}\text{-point between the } \Gamma \text{ and X points.}"

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References

[1] Cullis A G, Canham L T and Calcott P D J 1997 J. Appl. Phys. 82 909
[2] Wolkin M V, Jorne J, Fauchet P M, Allan G and Delerue C 1999 Phys. Rev. Lett. 82 197
[3] Cho E C, Park S, Hao X, Song D, Conibeer G, Park S C and Green M A 2008 Nanotechnology 19 245201
[4] Conibeer G et al 2006 Thin Solid Films 511 654
[5] Chiang W-J, Chen C-Y, Lin C-J, King Y-C, Cho A-T, Peng C-T, Chao C-W, Lin K-C and Gan F-Y 2007 Appl. Phys. Lett. 91 051120
[6] Huh C, Kim B K, Park B-J, Jang E-H and Kim S-H 2013 Nanoscale Res. Lett. 8 1
[7] Kim K 1998 Phys. Rev. B 57 13072
[8] Kanemitsu Y 1994 Phys. Rev. B 49 16845
[9] Wu X L, Fan J Y, Qiu T, Yang X, Siu G G and Chu P K 2005 Phys. Rev. Lett. 94 026102
[10] Rossi A M, Murphy T E and Reipa V 2008 Appl. Phys. Lett. 92 253112
[11] Li H et al 2010 Angew. Chem., Int. Ed. 49 4430
[12] van Buuren L N D T, Chase L L, Siekhaus W J and Terminello L J 1998 Phys. Rev. Lett. 80 3803
[13] Kurokawa Y, Tomita S, Miyajima S, Yamada A and Konagai M 2007 Japan. J. Appl. Phys. 46 L833
[14] Kim T-W, Cho C-H, Kim B-H and Park S-J 2006 Appl. Phys. Lett. 88 123102
[15] Kim S-K, Kim B-H, Cho C-H and Park S-J 2009 Appl. Phys. Lett. 94 183106
[16] Wilcoxon J P, Samara G A and Provencio P N 1999 Phys. Rev. B 60 2704
[17] Furukawa S and Miyasato T 1988 Phys. Rev. B 38 5726
[18] Chelikowsky J R, Zayak A T, Chan T L, Tiago M L, Zhou Y and Saad Y 2009 J. Phys.: Condens. Matter 21 064207
[19] Iwata J-I, Takahashi D, Oshiyama A, Boku T, Shirashi K, Okada S and Yabana K 2010 J. Comput. Phys. 229 2339
[20] Oshiyama A and Iwata J-I 2011 J. Phys.: Conf. Ser. 302 012030
[21] Garoufalis C S, Zdetsis A D and Grimes S 2001 Phys. Rev. Lett. 87 276402
[22] Vasileiev I, Ogit S and Chelikowsky J R 2001 Phys. Rev. Lett. 86 1813
[23] Molteni C, Martošek R and Parrot M L 2002 J. Chem. Phys. 114 5358
[24] Rinnert H, Jambois O and Vergnat M 2009 J. Appl. Phys. 106 023501
[25] Hartel A M, Gutsch S, Hiller D and Zacharias M 2012 Phys. Rev. B 85 165306
[26] Brongersma M L, Kid P G, Polman A, Min K S and Atwater H A 2000 Appl. Phys. Lett. 76 351
[27] Heitmann J, Müller F, Yi L, Zacharias M, Kovalev D and Eichhorn F 2004 Phys. Rev. B 69 195309
[28] Yu W, Feng H, Wang J, Dai W, Yu X, Zhang J, Lai W and Fu G 2014 Physica B 434 177
[29] Varshni Y P 1967 Physica 34 149
[30] Bludau W, Onton A and Heinke W 1974 J. Appl. Phys. 45 1846
[31] O’Donnell K P and Chen X 1991 Appl. Phys. Lett. 58 2924
[32] Pässler B 2001 J. Appl. Phys. 89 6235
[33] Pässler B 2002 Phys. Rev. B 66 085201
[34] Goedecker S and Colombo L 1994 Phys. Rev. Lett. 73 122
[35] Colombo L 1998 Comput. Mater. Sci. 12 278
[36] Kwon I, Biwas R, Wang C Z, Ho K M and Soukoulis C M 1994 Phys. Rev. B 49 7242
[37] Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, Suhr H and Seifert G 1998 Phys. Rev. B 58 7260
[38] Niquet Y M, Delerue C, Allan G and Lannoo M 2000 Phys. Rev. B 62 5109
[39] Ren SY and Dow JD 1992 Phys. Rev. B 45 6492
[40] Martonák R, Colombo L, Molteni C and Parrinello M 2002 J. Chem. Phys. 117 11329
[41] Rebrodo F A, Franceschetti A and Zunger A 2000 Phys. Rev. B 61 13073
[42] Vogl P, Hjalmarson H P and Dow JD 1983 J. Phys. Chem. Solids 44 365
[43] Bernstein N, Melh M, Papaconstantopoulos D A, Papanicolaou N I, Bazant M Z and Kaxiras E 2000 Phys. Rev. B 62 4477
[44] Delerue C, Lannoo M and Allan G 2001 Phys. Stat. Sol. (b) 227 115
[45] Goodwin L 1991 J. Phys.: Condens. Matter 3 3869
[46] Clark C D C, Dean P J and Harris P V 1964 Proc. R. Soc. London A277 312
[47] Ivashchenko V I, Shevchenko V I, Rusakov G V, Klymenko A S, Popov V M, Ivashchenko I A and Bogdanov E I 2002 J. Phys.: Condens. Matter 14 1799
[48] Ivashchenko V I, Turchi P E A, Shevchenko V I, Ivashchenko I A and Rusakov G V 2002 Phys. Rev. B 66 195201
[49] Ivashchenko V I, Turchi P E A, Shevchenko V I, Ivashchenko I A and Rusakov G V 2003 J. Phys.: Condens. Matter 15 4119
[50] Goodwin L, Skinner AJ and Pettifor DG 1989 Europhys. Lett. 9 701
[51] Bowler D R, Fearn M, Goringe M C, Horsfield A P and Pettifor D G 1998 J. Phys.: Condens. Matter 10 3719
[52] Winn M D, Rassinger M and Hafner J 1997 Phys. Rev. B 55 5364
[53] Okada Y and Tokunara Y 1984 J. Appl. Phys. 56 314
[54] McSkimin H J and Andrewat P 1964 J. Appl. Phys. 35 2161
[55] Grobman W D and Eastman D E 1972 Phys. Rev. Lett. 29 1508
[56] Taylor A and Jones R M 1960 Silicon Carbid:—A High Temperature Semiconductor ed J R O'Connor and J Smaltjens (Oxford: Pergamon) 147
[57] Lee D H and Joannopoulos JD 1982 Phys. Rev. Lett. 48 1846
[58] Humphreys R G, Bimberg D and Choyke W J 1981 Solid State Commun. 39 163
[59] Kaiser W and Bond W L 1959 Phys. Rev. 115 857
[60] Grimsditch M H and Ramdas A K 1975 Phys. Rev. B 11 3139
[61] Dean P J, Lightowlers E C and Wight D R 1965 Phys. Rev. 140 A352
[62] Himpsel F J, Veen V D and Eastman D E 1980 Phys. Rev. B 22 1967
[63] Takayama R, Hoshi T and Fujiiwa T 2004 J. Phys. Soc. Japan 73 1519
[64] Takayama R, Hoshi T, Sugabe T, Zhang S L and Fujiiwa T 2006 Phys. Rev. B 73 165108
[65] Efros A L and Efros A I 1982 Sov. Phys. Semicond. 16 772
[66] Brus L 1986 J. Phys. Chem. 90 2355
 Brus L E 1984 J. Chem. Phys. 80 4403
[67] Kayanuma Y 1988 Phys. Rev. B 38 9797
[68] Slack G A and Bartram S F 1975 J. Appl. Phys. 46 89
[69] Thurmond C D 1975 J. Electrochem. Soc.: Solid-State Sci. Technol. 122 1133
[70] Goldberg Y, Levinshtein M E and Rumyantsev S L 2001 Properties of Advanced Semiconductor Materials GaN, AlN, SiC, BN, SiC, SiGe ed M E Levinshtein et al (New York: Wiley) 93
[71] Jambois O, Rimbert H, Devaux X and Vergnat M 2006 J. Appl. Phys. 100 123504
[72] Watanabe H, Kawabata K and Ichikawa T 2010 IEEE Trans. Electron Devices 57 3084