Molecular dynamics simulation of icosahedral Si quantum dot formation from liquid droplets

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The present paper reports on molecular dynamics simulations of the formation process of Si quantum dots (Si QDs). Icosahedral Si QDs are formed spontaneously by freezing 274-, 280-, and 323-atom Si droplets. We find that the initialization of pentagonal channels leads into the overall icosahedral structure. We also study the melting behavior of the 280-atom icosahedral Si QD. We find that the melting point is reduced more than 15% compared with that of bulk Si. A possible approach to synthesize icosahedral Si QDs is discussed. The formation of the icosahedral structure could be expected in other systems characterized by tetrahedral bonding network.

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I. INTRODUCTION

Silicon quantum dots (Si QDs) are scientifically and technologically important semiconductor nanoparticles. Their optical properties and electronic structures vary dramatically with size and atomic arrangement.[1–7] For example, the peak position of photoluminescence can be tuned by controlling the size, and the intensity of photoluminescence is higher in amorphous Si QDs than in crystalline Si QDs.[4,5] It has also been suggested that the spin dephasing time and coherence in optical excitations can be tuned by controlling the symmetry of the atomic arrangement.[7] These facts stress the importance of understanding and controlling the structure of Si QDs. While the most stable structures are well understood in small Si particles by theoretical calculations,[8,9] the determination of the structures in the nanosize regime is a very hard task.[7,10,11]

The most stable morphology of rare gas, gold, and copper nanoparticles changes from fcc to decahedral to icosahedral, as the size decreases.[12–17] For Si, one can draw two analogies. First, the space lattice of bulk crystalline Si is fcc. Second, although the yield is quite low, decahedral Si QDs have been observed in samples prepared by the gas evaporation method.[18,19] It is then expected that small Si QDs can be formed in the icosahedral structure.

From a geometrical viewpoint, the icosahedral structure, which consists of 20 slightly distorted crystalline tetrahedra, each exposing one of four (111) facets, can be built in the framework of tetrahedral bonding.[20] The (111) facets have the lowest area density of dangling bonds so that the surface energy could be minimum. The stability of the icosahedral structure at 0 K is determined by the competition of the strain energy and the surface energy. Recent first-principles calculations have shown that icosahedral Si QDs (*i*-Si QDs) have lower structure energies than crystalline Si QDs (*c*-Si QDs) at least for diameters smaller than 2.77 nm.[7] However it is not clear whether such a structure really exists.

Previous theoretical and experimental studies in various systems have suggested that the formation process actually determines the morphology of a nanoparticle.[5,6,12–14,16,18,19,21] For example, by controlling experimental conditions, *c*-Si QDs or amorphous Si QDs can be selectively synthesized.[5,6] Given the situation, molecular dynamics (MD) simulation is a powerful technique to study the stable structure of Si QDs[11,12,14,21] because it enables us to investigate the formation process of Si QDs directly by following up the motion of Si atoms. In addition, the thermal stability of Si QDs can be investigated.

In the present paper, we study the formation process of Si QDs of diameters in the range of 2.17 to 2.31 nm by means of MD simulations. Long-time simulations show that *i*-Si QDs are formed spontaneously by freezing Si droplets. The formation of pentagonal channels plays an important role in the formation of *i*-Si QDs. We also find that the melting point of the *i*-Si QD of 2.20 nm in diameter is reduced more than 15% compared with that of bulk Si.

II. MODEL AND METHODS

As we shall show later, it takes more than 50 ns to produce *i*-Si QDs by freezing Si droplets. Phenomena of such a long time-scale are intractable via first-principles or tight-binding molecular dynamics (TBMD) simulations. A short time-scale simulation by the TBMD method has shown that a 281-atom Si droplet freezes into an amorphous Si QD,[11] that is, the system is trapped in some metastable state. In our MD simulations, Si atoms are modeled by the empirical Tersoff potential, which is known to reproduce structural properties well, including tetrahedral bonding networks in both crystalline and amorphous phases.[22–24] By choosing the empirical potential, we can perform simulations long enough to study the formation process of *i*-Si QDs. When one uses empirical potentials, it is necessary to consider the transferability of the potentials. We consider that the Tersoff model captures the essence for representing the structural properties of *i*-Si QDs from the following two physical insights based on the results of the first-principles calculations:[7] (1) *i*-Si QDs are constructed by covalent bonding, or tetrahedral bonding (not by metallic bonding which is observed in very small clusters); (2) the poor description of the energetics of surface reconstructions in the Tersoff model does not affect the overall icosahedral structure, because *i*-Si QDs expose (111) facets without surface reconstructions.

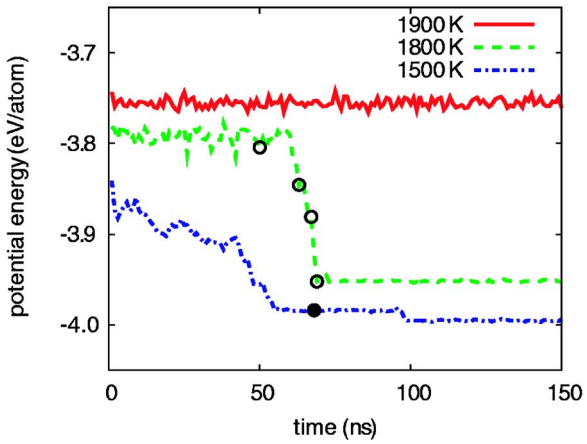

FIG. 1. (Color online) Time evolution of the potential energy for the 280-atom Si nanoparticle during the freezing procedure. The nanoparticle is liquidlike at 0 ns. The freezing transition takes place at 1500 and 1800 K. The snapshots of the atomic structures for the open circles and the filled circle are given in Figs. 2 and Fig. 3, respectively.

In our simulations, the temperature is controlled by the Nosé-Poincaré thermostat.[25] The equations of motion are solved with an explicit symplectic algorithm developed by Nosé.[26] The symplectic integrator is suitable for long-time simulations because it has good numerical stability compared with other nonsymplectic methods. The time step $\Delta t=0.5$ fs is used.

III. RESULTS AND DISCUSSION

A. Formation of 280-atom icosahedral silicon quantum dot

Liquid droplets are prepared by cutting out a bulk liquid Si equilibrated at 2500 K. The total linear momentum and total angular momentum around the center of mass are set to zero. After equilibrating at 2500 K, the droplet is annealed at 1500, 1800, and 1900 K. The temperature of the droplet reaches the desired value within several picoseconds after the temperature for the heat bath is changed from 2500 K. The potential energy averaged over 1 ns is calculated at intervals of 1 ns. The results for a 280-atom nanoparticle are shown in Fig. 1. The diameter of the 280-atom nanoparticle, defined as $d=(3Na^3/4\pi)^{1/3}$, is 2.20 nm. Here, N and $a=0.543$ nm are the number of Si atoms and the lattice constant of bulk crystalline Si, respectively. The potential energy fluctuates around a constant value at 1900 K. We have confirmed that no drastic change is observed until 1000 ns. On the other hand, at 1800 K, the potential energy drastically drops between 60 and 69 ns, showing that some kind of phase transition is taking place. Atoms moving around diffusively before the transition show only oscillation behavior around certain positions after the transition. In fact, mean atomic displacement in an interval of $\Delta t=0.1$ ns, $\langle|\boldsymbol{r}(t+\Delta t)-\boldsymbol{r}(t)|\rangle$, decreases considerably from 1.74 to 0.61 Å in this regime. These results suggest that the state of the nanoparticle changes from liquidlike to solidlike across the transition. As we shall discuss later, the snapshot at 69 ns shows that the solidlike nanoparticle is an *i*-Si QD. In contrast to the annealing procedure at 1800 K, the freezing transition proceeds gradually at 1500 K. Note that we have confirmed the reproducibility of the formation of the icosahedral structure by performing four additional simulations. Simulation times for the formation of the *i*-Si QD are 100 and 153 ns at 1500 K, and 145 and 319 ns at 1800 K.

The icosahedral structure consists of 20 slightly distorted crystalline tetrahedra. The edge atoms of the tetrahedra form 12 pentagonal channels.[7,20] In order to understand how randomly arranged Si atoms in a liquid state align themselves to form the icosahedral structure, we investigate the freezing process at the atomistic level. From our results, we find a common characteristic that the pentagonal channels play an important role in the formation process of *i*-Si QDs. We demonstrate in Fig. 2 the formation process of an *i*-Si QD at 1800 K as an example. In the liquid state, crystalline fragments frequently appear at arbitrary locations [Fig. 2(c)]. Such crystalline structures never grow to form a crystalline QD, but disappear. On the other hand, pentagonal channel fragments rarely appear in the liquid state. The situation is dramatically changed after 60 ns. The pentagonal channel fragments start to appear frequently, and the crystalline fragments, which are observed at arbitrary locations before 60 ns, frequently appear alongside of the pentagonal channels, leading to the formation of the tetrahedral fragments of the icosahedron. One of the 12 pentagonal channels is formed at 63 ns [Fig. 2(d)]. While the channel disappears at 67 ns, other channels are formed at different locations [Fig. 2(e)]. Seesawing back and forth, the formation of the pentagonal channels and the crystalline tetrahedra proceeds steadily, and a perfect *i*-Si QD is eventually formed at 69 ns [Fig. 2(f)].

The atomic rearrangement from a liquidlike disordered structure to a solidlike icosahedral structure proceeds rather gradually at 1500 K. The formation of an *i*-Si QD is almost completed at 55 ns (Fig. 1), but two structural defects still remain on the surface. One is caused by two excess atoms, shown in the upper right of Fig. 3. The other defect is caused by a shortage of two atoms. We can see in the middle of Fig. 3 that one pentagonal ring is not formed due to the shortage. These structural defects move around on the surface, and when they happen to meet each other, the formation of a perfect icosahedral structure is completed.

B. Favorability of icosahedral structure

In order to examine the favorability of the icosahedral structure more closely, we analyze the atomic configurations of solidlike nanoparticles made from a 274-droplet ($d=2.17$ nm) and a 323-atom droplet ($d=2.31$ nm). In these systems, we cannot make *i*-Si QDs without structural defects, due to the mismatch in the number of atoms. On the other hand, from a geometrical view point, 274 and 323 are the numbers of atoms for making perfect *c*-Si QDs with different faceting.[7] Nevertheless, the 274- and 323-atom droplets do not freeze into *c*-Si QDs, and *i*-Si QDs having surface defects are formed. In the 274-atom system, parts of the surface are incomplete due to the lack of six Si atoms [Fig.

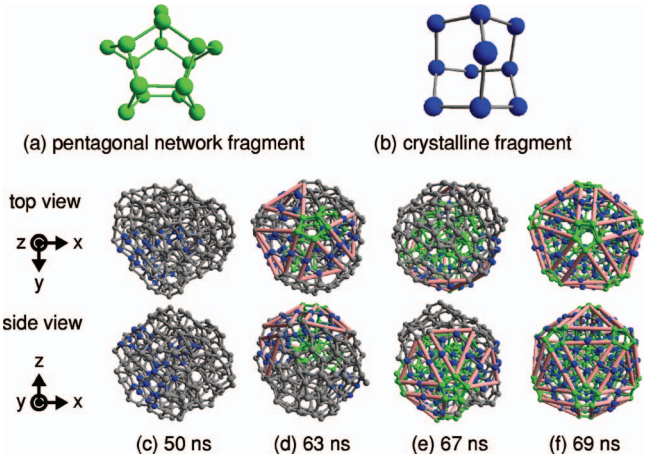

FIG. 2. (Color) Typical formation process of the *i*-Si QD. (a) pentagonal network fragment; (b) crystalline fragment; (c)–(f) snapshots of a 280-atom Si nanoparticle corresponding to the open circles in Fig. 1. Two snapshots from different angles are given in (c)–(f). Si atoms less than 2.85 Å apart are connected by bonds. Each atom and bond is colored according to the procedures described below. (1) All atoms and bonds are first shown in gray. (2) The atoms and bonds making up the pentagonal network fragment [shown in (a)] are in green. (3) The atoms making up the crystalline fragment [shown in (b)] are in blue. The (111) facets of the *i*-Si QD are indicated by light orange triangles for clarity. The same identifications are used in the other figures.

4(a)]. On the other hand, for the 323-atom QD, the 43 excess atoms form a part of the next shell on a perfect 280-atom *i*-Si QD [Fig. 4(b)]. The structural energies at 0 K evaluated by using the steepest decent method are −4.19 eV for the 274-atom *i*-Si QD and −4.20 eV for the 323-atom *i*-Si QD. These values are lower than those for the corresponding *c*-Si QDs: −4.05 eV (274-atom *c*-Si QD) and −4.16 eV (323-atom *c*-Si QD). Our findings that *i*-Si QDs are selectively made even from Si droplets having atoms for perfect *c*-Si QDs and that the *i*-Si QDs are energetically more stable than the *c*-Si QDs strongly suggest the preference for the icosahedral structure in this nanoparticle size regime.

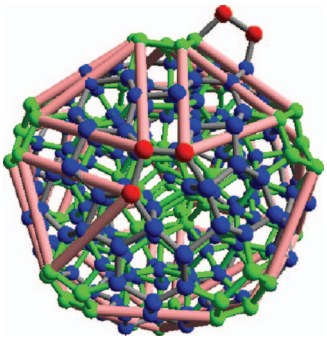

FIG. 3. (Color) The snapshot of a 280-atom Si nanoparticle corresponding to the filled circle in Fig. 1. Si atoms related to surface defects are shown in red for clarity. These defects move around on the surface. When they meet each other, the formation of the icosahedral structure is completed.

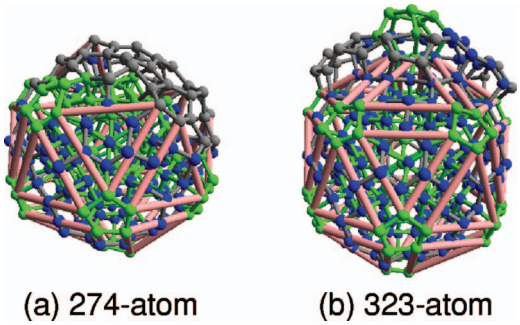

FIG. 4. (Color) Snapshots of (a) 274- and (b) 323-atom *i*-Si QDs. Although 274 and 323 are the numbers of atoms for perfect *c*-Si QDs, 274- and 323-atom droplets freeze into icosahedral structures with defects.

C. Melting behavior

In order to clarify the stability of the icosahedral structure, the perfect *i*-Si QD made from a Si droplet is kept at 1900 and 2000 K. The snapshots of the atomic configurations at 2000 K and the time evolution of the potential energy at 1900 and 2000 K are shown in Fig. 5. As shown in the snapshots, structural defects are formed frequently by thermal fluctuation (at 9 ns), but these defects are healed spontaneously (at 17 ns). The seesaw of defect formation and healing is observed until 118 ns. The melting transition eventually takes place at 118 ns, as a drastic increase in the potential energy indicates. The seesaw is also observed at 1900 K, but the *i*-Si QD does not melt in the time span examined.

The 280-atom droplet freezes into an *i*-Si QD at 1800 K, and the *i*-Si QD melts at 2000 K. These temperatures are the lower and upper bounds on the melting point T_m, respectively. We can thus estimate the melting point in a reduced unit as $0.76 < T_m/T_m^{bulk} < 0.85$, where $T_m^{bulk} = 2350$ K is the melting point estimated for bulk Si using the Tersoff model.[23] Considering the fact that the experimental melting

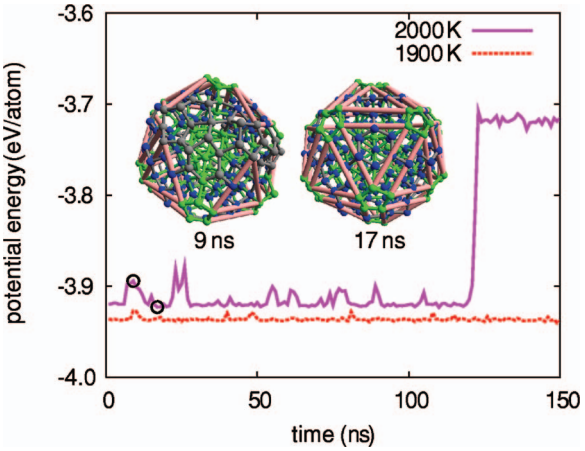

FIG. 5. (Color) Time evolution of the potential energy for the 280-atom Si nanoparticle during the melting procedure. The nanoparticle is a solidlike *i*-Si QDs at 0 ns. The melting transition takes place at 2000 K. Snapshots corresponding to the open circles at 9 and 17 ns in the 2000 K simulation are included.

point of bulk Si is 1685 K, the *i*-Si QD can be produced by controlling the temperature of Si nanoparticles below 0.85×1685 K $= 1432$ K.

D. Proposal for synthesis of icosahedral silicon quantum dots

Our MD simulations strongly suggest that icosahedral structures can be formed via a physical process. Contrary to the theoretical prediction, *i*-Si QDs have not been identified experimentally yet, in spite of the fact that there have been a considerable number of reports on synthesizing Si QDs including the size regime studied. The discrepancy may come from the differences in the surface conditions between our model system and experiments. In experiments, surface dangling bonds of Si QDs are usually terminated by hydrogen or oxygen atoms. The minimization of the surface energy, or the minimization of the number of dangling bonds plays an important role in the stability of the icosahedral structure. The termination of surface dangling bonds may enhance the stability of the crystalline structure compared with that of the icosahedral structure. Therefore, we suggest that a key for the synthesis of *i*-Si QDs is to prevent the surface termination until the formation of icosahedral structure completes. The minimization of the number of dangling bonds is determined by geometry so that the formation of the icosahedral structure is expected in other systems characterized by tetrahedral bonding network.

IV. SUMMARY

We have carried out MD simulations to study the formation process of Si QDs. Our results show that icosahedral Si QDs are formed spontaneously by freezing 274-, 280-, and 323-atom Si droplets. From the 280-atom droplet, the perfect *i*-Si QD is obtained. The 274- and 323-atom droplets freeze into icosahedral structures with surface defects, although 274 and 323 are the numbers of atoms for perfect *c*-Si QDs. The initialization of the pentagonal channels leads into the overall icosahedral structure. These results strongly suggest that *i*-Si QDs can be formed via a physical process. It is also found that the melting point of the perfect 280-atom *i*-Si QD is reduced more than 15% compared with that of bulk Si. A possible approach to synthesize *i*-Si QDs has been discussed. We have suggested that a key for the synthesis of *i*-Si QDs is to prevent the termination of surface dangling bonds until the formation of icosahedral structure completes. The minimization of dangling bonds, which is determined by geometry, plays an important role in the stability of the icosahedral structure so that the icosahedral structure is expected in other systems characterized by tetrahedral bonding network.

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