

Influence of Synthesis Conditions on the Structural and Optical Properties of Passivated Silicon Nanoclusters

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First-principles molecular dynamics and quantum Monte Carlo techniques are employed to gain insight into the effect of preparation conditions on the structural and optical properties of silicon nanoparticles. Our results demonstrate that (i) kinetically limited nanostructures form different core structures than bulk-derived crystalline clusters, (ii) the type of core structure that forms depends on how the cluster is passivated during synthesis, and (iii) good agreement with measured optical gaps can be obtained for nanoparticles with core structures different from those derived from the bulk.

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Silicon nanoclusters have been the focus of intense theoretical and experimental interest [1–4]. A combination of the unique optical properties of silicon quantum dots and their compatibility with existing silicon-based and nanobiological technologies demonstrates great promise for numerous applications. In the 1–3 nm size range, where Si quantum dots may exhibit visible luminescence, experimentally determined optical properties vary significantly depending on the synthesis technique [4–9]. For example, the optical gaps of silicon clusters formed by physical vapor deposition [10] were found to be several eV lower than those formed using inverse micelles [11]. Even quantum dots made via the same process have been found to exhibit widely varying absorption and emission spectra, perhaps due to small differences in preparation conditions and limitations in the accuracy of characterization techniques. These discrepancies pose a significant challenge to the practical application of silicon quantum dots and demonstrate the need for accurate theoretical predictions to help guide experiments.

Previous theoretical studies of silicon nanoclusters have used either bulk crystalline [12] or quasicrystalline structural templates [13] to generate atomic configurations. The highly curved surface is typically fully passivated with hydrogen to saturate dangling bonds. While these model structures allow for the study of a number of different properties (i.e., the effects of contamination and surface reconstruction), they do not allow one to examine the impact of the synthesis process itself. Investigating the synthesis process requires the use of computationally demanding quantum simulations in order to take into account the complex and subtle dynamical effects needed for accurate predictions.

In this Letter, we employ a combination of first-principles molecular dynamics (FPMD) and quantum Monte Carlo (QMC) calculations to determine the impact of the experimental synthesis process on the structural and optical properties of 1 nm silicon dots. Our results indicate that, when a finite-temperature synthesis and

passivation process is emulated, the number of atoms in the core of the resulting cluster is larger than for ideal, bulk-derived structures. We observe a subtle interplay between the strain associated with high curvature and surface dangling bonds and the preference for silicon to form tetrahedrally symmetric cores. These two competing effects produce a class of structures defined by the core geometry and the bonding of the core atoms to the surface. Rather than a search for low-energy structures, this classification results from a careful examination of the metastable, kinetically limited nanostructures produced by FPMD, and can be applied to other nanoscale systems. We also show that structures which are likely to form via a given synthesis method strongly depend on the mechanism by which the silicon surface is passivated and on the ability to satisfy surface strain during the growth sequence. In addition, we present novel nanoscale reconstructions, unique to highly curved crystalline structures, that have lower energy and larger optical gaps than the bulk-inspired reconstruction.

Several experimental techniques for synthesizing silicon nanoparticles, such as physical vapor deposition [10] and laser ablation [14], generate a high temperature silicon vapor from which amorphous nanoclusters nucleate as the vapor cools. During or after cooling, there is typically exposure to some form of passivant (e.g., hydrogen, oxygen) which removes dangling bond states from the surface of the cluster. In order to accurately account for bond breaking and formation processes during passivation, the Car-Parinello FPMD approach was employed [15], such that electronic degrees of freedom are solved quantum mechanically while the ions move classically. Starting from an amorphous cluster obtained by heating a bare cluster at 1500 K for ~ 2 ps, a new hydrogen atom is added to the surface every 0.3–0.5 ps until all silicon atoms are fourfold coordinated. Simple thermodynamic arguments, assuming atmospheric pressure and ideal gas vapor densities, predict an additional hydrogen will passivate the surface every 1–2 ps. By using a series of elevated temperatures ($T = 600, 800,$ and 1000 K), we

were able to observe realistic passivation events on shorter time scales (0.3–0.5 ps) while confirming that the higher temperatures did not qualitatively alter the growth process. For each system, multiple simulations were carried out from different starting points in order to obtain a statistically representative sample. The combined total simulation time for all clusters investigated here was ~ 500 ps.

The present work considers the 1 nm size range where there are ~ 30 silicon atoms per quantum dot. We performed simulations starting from amorphous Si_{29} and Si_{30} . Surprisingly, in our simulations which started from Si_{29} , the single tetrahedral core structure predicted for 29 silicon atoms [see Fig. 1(a)] does not form. Instead, we found that the resulting passivated structures consistently had a *double* tetrahedral core—two interior silicon atoms rather than one [see Fig. 1(b)]. The formation of a double core was found to be independent of temperature and the order in which hydrogen atoms were added to the surface. Eight separate synthesis calculations starting from amorphous Si_{29} all resulted in double-core structures.

The explanation for the consistent formation of a double-core structure lies with the dynamics of bare silicon clusters. Above $T = 300$ K, unpassivated crystalline nanoclusters become amorphous, with multiple atoms in the center of the cluster attempting to saturate the dangling bonds of the surface atoms. Clusters of amorphous Si_{29} typically have two to three such highly

coordinated interior atoms. As hydrogens are added to the surface, the number of dangling bonds is reduced and the interior atoms develop stable bonds to the surface. Passivation has the effect of “freezing” that region of the cluster surface as atoms at the surface become fourfold coordinated. By the time enough hydrogens have been added to fully passivate the surface, the surface has frozen around two interior core atoms. A transition from this type of structure to a single-core structure would likely require a global reconstruction of the surface, with multiple events involving the simultaneous breaking of several silicon bonds.

To quantify the degree to which a silicon atom is in the interior of the cluster, we estimate the fraction of the total solid angle around atom i that is not occupied by other silicon atoms. For simplicity, we approximate this solid angle by calculating the maximum base angle Ω of a cone whose apex is centered on atom i and whose volume does not intersect any other silicon atoms (see Fig. 2, inset). The quantity Ω is plotted vs time in Fig. 2 for a simulation of the synthesis of Si_{29} , starting from an unpassivated crystalline cluster. Within 0.5 ps, an atom has moved from the surface to become a second core atom in the cluster and remains there for the duration of the simulation.

By symmetry, 30 silicon atoms are energetically more favorable than 29 atoms for the formation of 1 nm double-core nanoclusters. $\text{Si}_{30}\text{H}_{22}$ has a symmetric construction which can be represented as a 28-atom cage (14 pentagons, 2 septagons) surrounding two interior atoms [Fig. 1(c)]. This structure was stable to thermodynamic

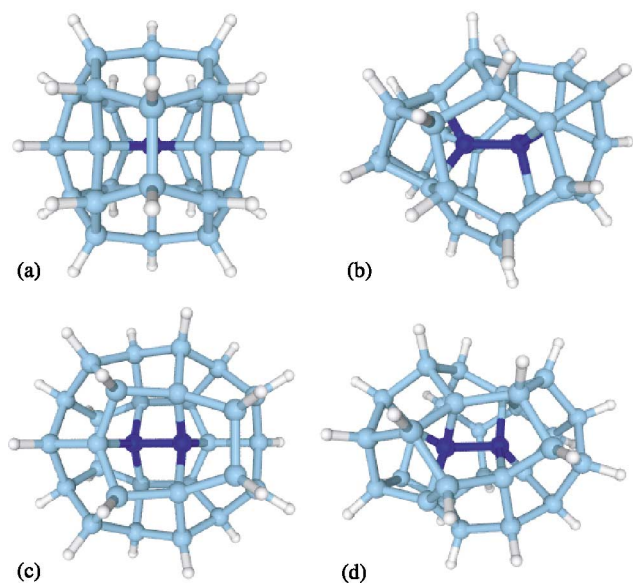


FIG. 1 (color). Results of FPMD synthesis for Si_{29} and Si_{30} , compared with low-energy ideal structures. Interior core atoms are dark blue. (a) Ideal $\text{Si}_{29}\text{H}_{24}$ structure proposed in Ref. [12]. (b) Representative final $\text{Si}_{29}\text{H}_{21}$ structure from FPMD synthesis at $T = 1000$ K, relaxed at $T = 0$ K. (c) Proposed ideal $\text{Si}_{30}\text{H}_{22}$ structure. (d) Representative final $\text{Si}_{30}\text{H}_{22}$ structure from FPMD synthesis at $T = 1000$ K, relaxed at $T = 0$ K.

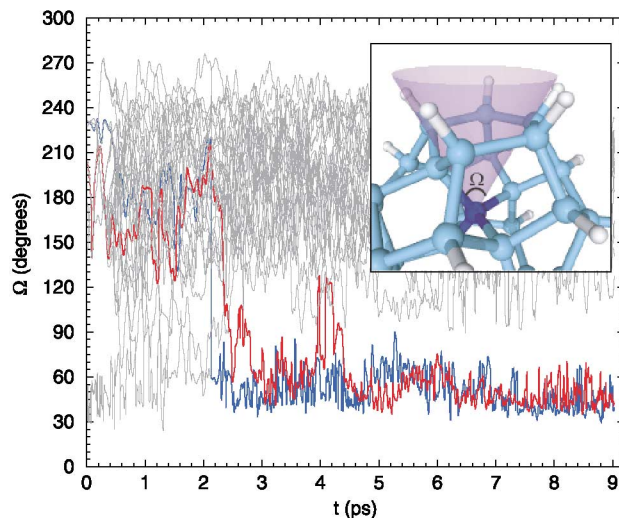


FIG. 2 (color). Maximum solid angle unoccupied by other silicon atoms Ω_i (see text) vs time in an Si_{29} FPMD synthesis run at $T = 1000$ K, after 2 ps at $T = 1500$ K, with a hydrogen atom added to the surface of the cluster every 0.3 ps. The blue and red curves correspond to the two final interior core atoms, and the grey curves are surface silicon atoms. The inset shows how Ω is defined, in this case for an interior atom (dark blue).

fluctuations at $T = 1000$ K for 10 ps. Six subsequent simulations of hydrogen passivation of amorphous Si_{30} at $T = 600$ and 1000 K, using the same FPMD synthesis calculations as for Si_{29} , again consistently produced double-core structures. Whereas for Si_{29} they were markedly different than the ideal case, for Si_{30} FPMD produced many low-energy structures [the example shown in Fig. 1(d) is only 0.1 eV higher in energy than the ideal structure Fig. 1(c)] that are qualitatively similar to the ideal high-symmetry structure.

As mentioned, a number of different experimental synthesis processes have been used to make silicon quantum dots. Recently, silicon nanoclusters with discrete cluster sizes have been produced by sonification of porous silicon [16]. In this process, silicon clusters are formed from larger pieces of hydrogenated silicon—a fundamentally different synthesis process to the silicon vapor based techniques described above, since the starting point is crystalline bulk, not amorphous vapor. The stability of the partially passivated surface of the resulting crystalline fragments to thermal fluctuations will impact the final structures produced by this type of process.

To determine the number of hydrogens required to maintain a single-core crystalline structure in a 29-atom silicon cluster, we performed FPMD simulations in which a number of neighboring hydrogen atoms were removed from a tetrahedrally symmetric $\text{Si}_{29}\text{H}_{24}$ nanocrystal. The cluster was then heated to $T = 600$ and 1000 K. At $T = 1000$ K, removal of only six hydrogen atoms ($\text{Si}_{29}\text{H}_{18}$) resulted in a persistently stable, single-core structure. When 12 hydrogen atoms were removed ($\text{Si}_{29}\text{H}_{12}$), the silicon cluster formed a double core within 0.5 ps. When 18 hydrogen atoms were removed (Si_{29}H_6), the cluster again formed a double core within 0.5 ps, but also exhibited dynamics consistent with an amorphous cluster, as shown by the exchange of interior core and surface atoms on a time scale of roughly 1 ps [Fig. 3(a)]. We found that 14 neighboring hydrogen atoms ($\text{Si}_{29}\text{H}_{14}$) are required to maintain a single tetrahedral core. At $T = 600$ K, similar behavior is observed, although the double core formed more slowly than at $T = 1000$ K. These findings suggest that the retention of a crystalline core depends on both the fraction of dangling bonds at the surface and the passivation time scale.

Assuming the 1 nm nanoclusters formed with porous sonification are in fact crystalline, the measured optical gaps are not in agreement with the gap of the lowest-energy crystalline $\text{Si}_{29}\text{H}_{24}$ structure. A bulklike surface reconstruction of crystalline $\text{Si}_{29}\text{H}_{36}$ to $\text{Si}_{29}\text{H}_{24}$ was proposed [12] [see Fig. 1(a)] and found to have an optical gap in agreement with an experimentally measured optical gap of 3.44 eV for 1 nm clusters synthesized using porous sonification [16]. Here we present two lower-energy reconstructions of $\text{Si}_{29}\text{H}_{24}$ with optical gaps significantly larger than 3.5 eV. The surface of a $\text{Si}_{29}\text{H}_{24}$ cluster can be represented as a 28-atom cage (12 pentagons, 4 hexagons)

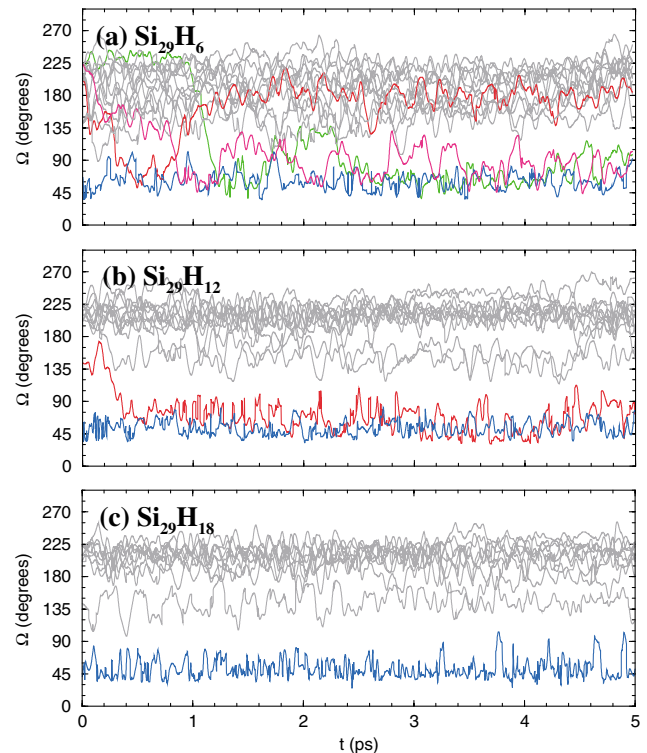


FIG. 3 (color). Interior parameter Ω_i vs time for the silicon atoms in (a) Si_{29}H_6 , (b) $\text{Si}_{29}\text{H}_{12}$, and (c) $\text{Si}_{29}\text{H}_{18}$ FPMD simulations at $T = 1000$ K. The colored curves correspond to atoms which are in the interior of the cluster at some point in the simulation, and the grey curves are surface atoms.

with a single silicon atom in the center, bonded to four surface atoms (related by T_d symmetry) to form a five-atom tetrahedral core. The remaining surface atoms are passivated with hydrogen. There are three unique ways to connect the interior core atom to the surface and maintain a tetrahedral core. The first [$\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$, Fig. 1(a)] was proposed based on a bulklike (2×1) reconstruction of dimer pairs on (001) facets. The other two (Fig. 4), $\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$ and $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$, are *unique to a curved nanostructure*, and have no bulk analogue. Two similar reconstructions exist for ideal $\text{Si}_{30}\text{H}_{22}$ [Fig. 1(c) shows the lowest energy structure].

To calculate energy differences and optical gaps that are directly comparable with experiment, we employ the highly accurate fixed-node diffusion Monte Carlo (DMC) method. In our DMC approach [17–19], we use an optimized many-body trial wave function which is a product of Slater determinants and a correlation factor; we use nonlocal pseudopotentials to treat atomic cores, and fixed geometries taken from FPMD calculations. The DMC energies of $\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$ and $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$ are 0.6(1) and 1.0(1) eV lower than $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$, respectively, due to decreased strain around the surface dimers. In fact, a partial reconstruction from $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$ to $\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$, in which a single surface core atom takes the hydrogen from its neighbor which then bonds to the central core atom,

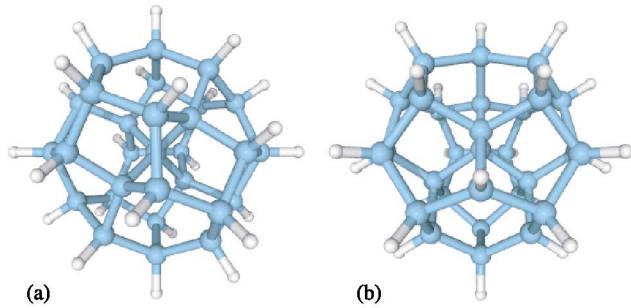


FIG. 4 (color). Two different reconstructions of a $\text{Si}_{29}\text{H}_{24}$ nanocluster: (a) $\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$; (b) $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$.

also has lower energy than $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$. Therefore, the full reconstruction from $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$ to $\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$ only involves the breaking of a single silicon bond at a time.

In addition to energy differences, we also employ QMC to calculate optical gaps in the same manner as in Ref. [20]. Table I lists both density-functional theory (DFT) and QMC optical gaps for different structures considered here. While only the QMC results are expected to be directly comparable to experimental absorption data, note that the DFT gaps accurately reproduce the QMC trends. A range of DFT gaps for clusters generated by FPMD synthesis is provided to give an estimate of statistical variation of the results, and the corresponding QMC gaps of structures produced with FPMD are consistently in good alignment with experiment [9,16]. It is interesting to note that structures with a double core consistently have similar gaps, between 3.2 and 3.4 eV, regardless of symmetry, size, or stoichiometry. In contrast, the optical gap calculated with QMC for single-core $\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$ is 4.5(1) eV and for $\text{Si}_{29}\text{H}_{24}^{\text{nano2}}$ is 4.1(1) eV, significantly larger than the 3.5(1) eV gap of $\text{Si}_{29}\text{H}_{24}^{\text{bulk}}$ and current experimental measurements.

In summary, we find that during the formation process of 1 nm clusters, relaxation of the high strain induced by the curvature and dangling bond states at the surface is in direct competition with the preference of the interior atoms to be tetrahedrally coordinated. Our results show that the resulting structures consistently have a noncrystalline, double tetrahedral core, with optical gaps in good agreement with experimental measurements, illustrating

TABLE I. Energy gaps for silicon nanoclusters, calculated using both DFT and QMC. For structures created with FPMD, a range of DFT gap energies is given, with QMC gaps calculated only for the structure with the largest DFT gap.

	$E_{\text{gap}}^{\text{DFT}}$ (eV)	$E_{\text{gap}}^{\text{QMC}}$ (eV)
$\text{Si}_{29}\text{H}_{22}^{\text{FPMD}}$	2.2–2.3	3.3(1)
$\text{Si}_{29}\text{H}_{24}^{\text{nano1}}$	3.1	4.5(1)
$\text{Si}_{30}\text{H}_{22}^{\text{FPMD}}$	2.2–2.4	3.4(1)
$\text{Si}_{30}\text{H}_{22}^{\text{ideal}}$	2.2	3.2(1)

that in some cases noncrystalline clusters may in fact be responsible for experimentally observed luminescence. We find reconstructions unique to highly curved nanostructures which give evidence for larger optical gaps than previously predicted in reconstructed 1 nm crystalline nanoclusters. In addition, we find that the stability of small, partially passivated Si_{29} crystalline fragments strongly depends on the number of hydrogen atoms at the surface, with a crossover from double-core to single-core structures between 12 and 14 hydrogen atoms. This work suggests that the metastable nanostructures most likely to form via a given synthesis process should be classified in terms of both core structure and surface reconstruction.

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