Surface control of optical properties in silicon nanoclusters

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Density functional and quantum Monte Carlo calculations are employed to determine the effect of surface passivants on the optical gap of silicon nanoclusters. Our results show that quantum confinement is only one mechanism responsible for visible photoluminescence and that the specific surface chemistry must be taken into account in order to interpret experimental results. Significant changes occur in the optical gap of fully hydrogenated silicon nanoclusters when the surface contains passivants that change the bonding network at the surface. In the case of just one double-bonded oxygen atom, the gap reduction computed as a function of the nanocluster size demonstrates that one contaminant can greatly alter the optical gap. A further significant reduction of the gap occurs with multiple double-bonded oxygen contamination, providing a consistent interpretation of several recent experiments. We predict that other passivants that distort the tetrahedral bonding network at the surface, including other double-bonded groups and in some cases bridged oxygen, will also significantly affect the optical gap. Conversely, single-bonded passivants will have a minimal influence on the optical gap. A discussion of the difference in the strength of the optical transitions for clusters with different passivants is presented. © 2002 American Institute of Physics. [DOI: 10.1063/1.1504707]

I. INTRODUCTION

The field of research surrounding the optical properties of semiconductor nanoclusters has seen enormous growth over the last decade.1–3 As the dimensions of a semiconductor are reduced to the nanometer scale, below its exciton Bohr radius (the strong confinement regime), the optical gap increases significantly due to quantum confinement. Several experiments have reproduced the one-to-one correspondence between the size and the wavelength of absorbed and emitted visible light in II/VI semiconductor nanostructures such as CdSe.4,5 This reproducibility has generated excitement for the possibility of using these clusters in emerging technologies such as biological markers and nanostructure lasers. Other semiconductor nanoclusters, specifically those in group IV such as silicon and germanium, are also known to absorb and emit visible light when their size is reduced to the nanometer scale.4–8 The efficient photoluminescence (PL) observed in porous silicon4 as well as in free standing nanoclusters5–7 suggest that these structures may serve as an alternative for CdSe in certain applications. One benefit of exploiting the optical properties of silicon nanoclusters over CdSe is the potential of silicon nanoclusters to be integrated within existing silicon technologies in order to create nanoscale optoelectronic devices. Additionally, the biocompatibility of silicon makes it an ideal candidate for replacing fluorescent dyes as biotags. However, the size dependence of the optical gap in silicon nanoclusters has so far been difficult to reproduce experimentally, as surface effects play a prominent role, the majority of atoms in these structures being at or near the surface. Developing a thorough understanding of the electronic and optical properties of silicon nanoclusters, in particular the effect of the surface on their optical properties, is a crucial step towards the utilization of these particles for new technologies.

Most experiments designed to explore the optical properties of semiconductor nanoclusters have focused on II/VI materials such as CdSe, CdS, and CdTe (Refs. 1, 2, and 9–11) as these clusters can be easily synthesized with a narrow size distribution and with well passivated surfaces. In contrast, the synthesis of covalently bonded nanoparticles, e.g., silicon, has proven much more challenging. Therefore, silicon clusters are much less well characterized than II/VI compounds and the interplay of quantum confinement and surface properties is still unclear. In particular, few surface sensitive probes are available, and distinguishing bulk effects from surface effects is difficult. Theoretical modeling12–16 is challenging within this size regime as a full quantum mechanical description of both the core and the surface atoms is required to provide accurate and predictive data. Specifically, as many silicon nanoclusters are synthesized in the presence of air, the role of oxygen in such synthesis processes has generated some controversy. The school of thought advocating quantum confinement as the only mechanism responsible for PL would suggest that regardless of the passivating surface, the same results should be observed as long as all dangling bonds are saturated,17–19 similar to observations in CdSe. Recent studies have shown that the surface can affect the optical properties including gaps and radiative lifetimes (i.e., the strength of transition).20–22 Therefore, the possibility for surface control of optical properties provides opportunities to design nanoclusters with desired characteristics.

In this paper, we present ab initio calculations of a number of hydrogen passivated silicon nanoclusters with diameters up to 2 nm. In our calculations, we replaced one or more of the hydrogen atoms with a number of different pas-
sivants including oxygen, sulfur, CH₂, fluorine, chlorine, and a hydroxyl group (OH). We found that any passivant that distorts the tetrahedral sp³ network reduces the gap significantly compared to that of a completely hydrogenated cluster. Such passivants include any double bonded passivant, or oxygen in particular bridged networks. We find that more than one of these passivants on a single cluster reduces the gap even further. Conversely, we show that single-bonded passivants have a minimal effect on the optical gap, but may affect the strength of optical transitions, the radiative lifetimes, and thus the quantum yield. We present results demonstrating that the most likely way for oxygen to bond to the surface depends on the size of the cluster. In a double-bonded network, we calculate the size below which an “oxygen gap” will be observed. These results may provide an explanation for the discrepancies found in recent experiments.5,17–19,23,24

The rest of this paper is organized as follows: Section II discusses the theoretical methods we used to perform our calculations. Sec. III discusses the effect of different surface passivants at one size, Sec. IV demonstrates how size affects the optical gap of clusters with different passivants. Sec. V suggests how oxygen bonds in different networks, Sec. VI then examines the effect of multiple-oxygen contamination in these various networks, and finally Sec. VII offers some concluding remarks.

II. COMPUTATIONAL METHODS

Our large scale ab initio calculations, capable of covering a range of silicon nanoclusters up to 2 nm in diameter, were performed using density functional theory (DFT) and quantum Monte Carlo (QMC). Our DFT calculations are based on the local density approximation (LDA) using the Ceperley–Alder exchange-correlation functional and potential25 and the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.26 We employed a pseudopotential plane wave approach27 with periodic boundary conditions applied to a supercell with a large enough spacing so that no interactions existed between the periodic replica. All the clusters are placed in a box with 9 to 16 Å of vacuum region between clusters (the precise amount depends on the resulting structural relaxation of the clusters with the different passivants and on convergence tests performed for each system). This amount of vacuum proved sufficient for the total charge density to approach zero (<10⁻⁷) well before the supercell edge. The interactions between the silicon ionic cores and the valence electrons are described by a fully norm conserving, nonlocal pseudopotential of the Hamann type,28 except for hydrogen in which we used a pseudopotential of the Gianozzi type.29 The Kohn–Sham orbitals are expanded in a plane wave basis set, \( \psi(r) = \sum G C_G \exp(iG \cdot r) \), where \( C_G \) is the Fourier coefficient, \( G \) is a three dimensional reciprocal lattice vector, and \( r \) is the three-dimensional coordinates in real space. The kinetic energy cutoff used is about 10⁵ Ry corresponding to about 10⁵ plane waves in a cell of 41 to 46 a.u. per side. In cases with passivation groups different from hydrogen, we used up to 70 Ry for convergence tests. We found that the higher cutoff had a negligible effect (less than 0.3% in all cases) on the difference between eigenvalues of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), that is, the single-particle gap as defined within DFT.

All silicon clusters were initially constructed on a diamond structure lattice with bulk silicon–silicon bond lengths. Dangling bonds were passivated with hydrogen placed along the appropriate tetrahedral direction at the experimental silicon–hydrogen distance in SiH₄. The structures were then relaxed to zero temperature using molecular dynamics simulations, with the ions treated classically and the electrons quantum mechanically, until the correct ground state structure was reached. In every case, each atom was relaxed until the residual forces on all atoms were less than 2 \( \times 10^{-4} \) eV/Å. We also performed GGA calculations on a number of representative clusters, including full geometry reoptimization, in order to test the effect of gradient corrections in the exchange-correlation potential. Despite slight changes to the structure (e.g., 1.6% longer silicon–silicon bond lengths), the single particle gaps agree to within 0.05 eV with LDA gaps for all cases tested.

Although the LDA HOMO/LUMO gap has been shown to qualitatively reproduce trends of optical gaps, a proper treatment of the self-energy and the exciton binding energy (Coulomb interaction between the excited electron and its resulting hole) requires a more accurate tool to quantitatively calculate optical gaps. For this purpose, we adopt the fixed node, diffusion quantum Monte Carlo (DMC) method,30–32 in which one solves the many-particle, imaginary time Schrödinger equation

\[
-\frac{\partial}{\partial t} \Phi(R,\tau) = (\hat{H} - E_T)\Phi(R,\tau),
\]

where \( \tau \) is imaginary time, \( R = (r_1, r_2, ..., r_n) \) is a configuration of electron coordinates in real space, \( \hat{H} \) is the many-body Hamiltonian of the system, and \( E_T \) is a trial energy. Representing the Schrödinger equation in this form allows it to be stochastically sampled when recast in integral form. The true ground state wave function is then projected out from a suitably chosen trial wave function. Our trial wave functions are of the Slater–Jastrow form with one-, two-, and three-body terms expanded as Chebyshev polynomials.33

\[
\Psi = D^1 D^1 \exp \left[ \sum_{i=1}^{N} \chi(r_i) + \sum_{i<j}^{N} u(r_i, r_j, r_{ij}) \right].
\]

We use the recently implemented linear scaling QMC approach,31 which constructs the Slater determinants, \( D^1 \) and \( D^1 \), from a set of maximally localized Wannier functions.34 The one-body, \( \chi \), and Jastrow \( u \) functions contain 18 to 40 variational parameters which are optimized using the variance minimization approach.35,36

Within the QMC approach it is possible to calculate two classes of gaps, the quasiparticle gap, \( E^{QP} \), and the optical gap, \( E^{opt} \), which are defined as

\[
E^{QP} = E_{N+1} - E_{N-1} - 2E_N,
\]

\[
E^{opt} = E^*_N - E_N,
\]

where \( E_N, E_{N+1}, \) and \( E_{N-1} \) are the ground state total energies of the system with \( N \) electrons filling all the occupied
states, with an additional electron added to the system and an electron removed from the system. $E_\text{gs}$ is the total energy of the system in an excited state where an electron has been excited from an occupied (valence) orbital to an unoccupied (conduction) orbital.

The quasiparticle gap represents the difference between the ionization potential and electron affinity of a system. It includes the self-energy corrections to the conventional single-particle density functional gap. It is equivalent to the first pole of the Green’s function for the system as calculated within many-body Greens function-screened potential (i.e., GW) techniques. As QMC is a full many-body formalism, quasiparticle gaps calculated within QMC do not suffer from the LDA “band gap problem,” even if the nodal structure for the QMC wave function is constructed from LDA orbitals.

When calculating an optical gap, one calculates the total energy of the excited system, $E_{\text{gs}}^\text{x}$. In this system both the excited electron and the resulting hole introduced into the valence band are present in the system at the same time. This excited electron and hole interact via the Coulomb interaction, producing an exciton binding. The optical gap of a system corresponds to the energy required to excite an electron into the conduction band, for example, by the absorption of a photon within an absorption experiment. In this paper, all QMC values for gaps refer to the optical gap as we believe this is the appropriate quantity to compare with the optical measurements examined here.

A QMC calculation of the optical gap using Eq. (3) only provides information on the size of the energy gap—it does not predict the strength of the interaction with a photon supplying the excitation energy, i.e., the dipole oscillator strength. To make contact with the wide range of experimental methods used to ascertain optical gaps, ranging from simple PL measurements to x-ray absorption spectra (XAS), the calculation of the strength of a given transition is of paramount importance. QMC methods cannot routinely be used to generate absorption spectra. Other methods, such as time-dependent-LDA (TD-LDA) or solving the Bethe–Salpeter equation (BSE), are more appropriate to generate such spectra. However, we can estimate the relative strength of a given transition by calculating dipole matrix elements,

$$f_{ij} = \frac{2m\omega_{ij}}{3\hbar} \sum_{k=1}^{3} \left[ \psi_f^*(x_1,x_2,x_3) \delta_{k} \psi_i(x_1,x_2,x_3) d^3r \right]^2,$$

where $\psi_f^*$ ($\psi_i$) are the final (initial) LDA states, $x_k$ are the three Cartesian directions, used here instead of only one direction as silicon clusters with different contaminants will not be spherically symmetric, and $\omega_{ij}$ is the frequency of transition. Because our adopted supercell size is large, each $\psi$ is essentially zero ($< 10^{-5}$) at the box edge. Thus, by integrating over the box in real space, we essentially integrate to $\infty$, and a reasonable estimate of transition (i.e., oscillator) strength is obtained within the accuracy of an LDA pseudopotential based calculation. From the oscillator strengths, we can obtain a comparative estimate of excitonic lifetimes through the relationship

$$\frac{1}{\tau} = \frac{e^2}{2\pi m c^3} \omega_{ij}^2,$$

where $e$ is the electron charge, $m$ is the electron mass, $c$ is the speed of light, and $\omega_{ij}$ is a model dielectric constant. For lifetime estimates in silicon clusters, we use a generalization of the Penn model in order to obtain the dielectric constant of particular silicon nanoclusters.

### III. EFFECT OF DIFFERENT SURFACE PASSIVANTS

The effect of different passivants on silicon nanoclusters was studied by replacing a single hydrogen with a number of different single-bonded species, two hydrogen atoms with a number of double-bonded species, and additionally, in the case of oxygen, two hydrogen atoms with a bridged oxygen (Si–O–Si). The effect of multiple oxygen contamination was studied by replacing pairs of hydrogens with oxygen in a variety of bridged and double-bonded configurations. The effect of these various passivants on the HOMO/LUMO gap was initially studied within the LDA. Although not quantitatively accurate, the LDA provides a methodology for testing a wide range of systems, whereas QMC provides a quantitative tool to make predictions directly comparable with experiment. LDA also allows one to probe the density of the orbitals closest to the Fermi level, thus generating insight into the states involved in the optical transitions.

The effect of changing the surface chemistry was initially tested on $\text{Si}_{35}\text{H}_{36}$ (diameter 1.1 nm) for a range of passivants. The passivants tested here include those commonly studied in experiments, e.g., oxygen. Keeping the entire cluster intact, we replaced a single hydrogen with the highly electronegative fluorine atom, which is present in HF, commonly used for etching porous silicon. Other highly electronegative species such as chlorine and an OH group were also considered. In addition to having similar properties to fluorine, chlorine is used often as a precursor in colloidal synthesis of silicon nanoparticles, while OH is a possible passivant of nanoclusters synthesized in atmosphere or in a...
peroxide solution. Figure 1(a) shows the density of states (DOS) of each of these systems. The DOS profiles for the clusters with single-bonded passivants (H,F,Cl,OH) are virtually identical, indicating that most single-bonded passivants are likely to generate similar single-particle gaps, regardless of their electronegativity or individual atomic levels. The triple degeneracy of the HOMO found in a totally hydrogenated cluster with Td symmetry is broken when a single contaminant is introduced, giving rise to a small splitting. As shown in Fig. 2(a), the probability density of the HOMO and the LUMO of Si35H36 are both confined to the core of the cluster. This confinement is similar to that seen in clusters with single-bonded passivants. Using chlorine as an example [see Fig. 2(b)], we see that although the HOMO and LUMO densities are altered with respect to the fully hydrogenated cluster, the bulk of the HOMO and LUMO density remains core confined.

The effect a single-bonded passivant has on the strength of the lowest transitions was calculated through Eq. (3), the results of which are given in Table I. Surprisingly, we see that a single-bonded passivant such as chlorine, fluorine, or a hydroxyl group significantly increases the strength of the lowest lying HOMO/LUMO transition compared with purely hydrogen passivated clusters (Si35H36). Because excitonic lifetimes are inversely proportional to the oscillator strength, single-bonded passivants other than hydrogen could induce a greater quantum yield without altering the gap as the shorter excitonic lifetimes would allow recombination before other effects (such as Auger transitions) could occur. An estimate of the lifetimes through Eq. (4) shows a lifetime of as much as \( \approx 250 \) ns with no contaminants, while a single passivant such as chlorine or fluorine will decrease the lifetime to \( \approx 40 \) ns. These shorter lifetimes could account for the high quantum yields observed in experiments where ligands are used to passivate the surface of silicon nanoclusters.7

The second set of passivants considered here are those forming a double (\( \pi \)) bond with a surface silicon atom. In addition to the common contaminant oxygen, we considered sulfur and CH2. The effects of the double-bonded passivants on the HOMO/LUMO gap are profound [see Fig. 1(b)], with the LDA gap decreasing from the completely hydrogenated case by an amount ranging from 0.9 eV (when CH2 is added) to 1.6 eV (when sulfur is added). These results show that quantum confinement may not be the only mechanism responsible for the visible PL in silicon nanoclusters, and offer an explanation of the discrepancies in the measured values of the optical gap between many experiments performed in the presence of oxygen.6,17,20,23 In smaller clusters (< 2 nm), the actual transition may involve localized oxygen states.

The closing of the gap due to double-bonded passivants was further investigated by examining the HOMO and LUMO densities. Figure 2(c) shows that these states in Si35H34O are localized around the double bond with little of the core confinement seen in the Si35H35Cl cluster. This localization suggests that these states might be pinned at a fixed energy determined by the oxygen atom and relatively independent of the size of the cluster.

Next, we examined whether the smallest gap in double-bonded passivants can be observed. With this aim, we calculated the lowest transitions of Si35H34O and Si35H34S (see Table I). For double-bonded passivants such as oxygen and sulfur, the lowest lying transition is negligible; however, the HOMO-1/LUMO transition is strong, an order of magnitude larger than that of the completely hydrogenated cluster in the oxygen contaminated cluster. GW-BSE calculations show this HOMO-1/LUMO transition to be 0.2 eV larger than the HOMO/LUMO transition in Si10 clusters with one oxygen.39 In the cluster with the sulfur contamination, this transition is three times stronger than the same transition in the cluster with a single oxygen contaminant. Such a strong transition would yield excitonic lifetimes on the order of \( \approx 2 \) to 3 ns.

### IV. SIZE DEPENDENCE OF THE EFFECTS OF DIFFERENT PASSIVATIONS

The size dependence of the effect of oxygen passivation on the optical properties of hydrogenated silicon nanoclusters was carried out in silicon clusters with pure hydrogen termination and in silicon clusters with a single oxygen atom, double bonded to the surface. Figure 3 shows the values of the LDA HOMO-LUMO gap (solid circles and

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**TABLE I. Oscillator strength calculation (unitless quantity) for 1 nm clusters with various passivants for transitions from the highest occupied molecular orbital (HOMO) and the two states below, to the lowest unoccupied molecular orbital (LUMO).**

<table>
<thead>
<tr>
<th>Cluster</th>
<th>HOMO/LUMO</th>
<th>HOMO-1/LUMO</th>
<th>HOMO-2/LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si35H36</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>Si35H35Cl</td>
<td>0.062</td>
<td>0.071</td>
<td>0.044</td>
</tr>
<tr>
<td>Si35H35OH</td>
<td>0.076</td>
<td>0.016</td>
<td>0.051</td>
</tr>
<tr>
<td>Si35H35F</td>
<td>0.053</td>
<td>0.018</td>
<td>0.070</td>
</tr>
<tr>
<td>Si35H35S</td>
<td>0.00</td>
<td>0.340</td>
<td>0.069</td>
</tr>
<tr>
<td>Si35H35O</td>
<td>0.00</td>
<td>0.119</td>
<td>0.077</td>
</tr>
</tbody>
</table>
defined as close to the oxygen double bond "oxy-
gap," formed by transitions between the states localized
ment. For clusters smaller than 1.8 nm in diameter, the "oxy-
us, demonstrating the key role played by quantum confine-
ments. Extrapolation of our QMC calculations for the optical gap of hydrogenated Si clusters with and
associated with the passivant are in the gap for sizes much
smaller than 1.1 nm. We examined this possibility by study-
ings smaller clusters passivated with a single fluorine atom,
comparing the results with similar clusters completely
hydrogenated, or with one double-bonded oxygen. As seen in
Fig. 4, the HOMO and the LUMO of clusters containing
fluorine follows a similar trend as that of the completely
hydrogenated cluster as a function of size, with a slightly
lower LUMO and slightly higher HOMO of hydrogenated
clusters. This behavior is significantly different from that
found for the smaller oxygen passivated clusters that exhibit
a weaker size dependence of their optical gaps and thus have a gap close to
constant.

The fluorine, chlorine, and OH results indicate that the
electron negativity of a passivant does not play a key role in
altering the gap. The fact that OH does not alter the gap
indicates that lone pair states are, in general, not responsible
for the reduction observed by the presence of oxygen. This
conclusion is further supported by the results obtained for
custers passivated with CH3 which has no lone pair when
double bonded to the cluster, yet closes the gap significantly
more than all the single-bonded passivants. The presence of a
double bond induces a considerable distortion of the tetrahe-
dral \( sp^3 \) network of the cluster and it is therefore possible
that this distortion is responsible for a gap reduction. In order
to test this conjecture, we distorted the bond angle between
two hydrogen atoms in silane. Figure 5 summarizes these
findings. A slight \((10^\circ)\) change of one H–Si–H angle can
close the gap significantly (tenths of an eV) while the result-
ing increase in the total energy is small (a few meV). These
results indicate that any distortion of the \( sp^3 \) network will

FIG. 3. Local density approximation (LDA) and quantum Monte Carlo (QMC) calculations for the optical gap of hydrogenated Si clusters with and without oxygen as a function of size. The curves are fit to the points and to
the bulk value and have been extrapolated to estimate the crossing point
beyond which the "oxygen gap" will no longer be observed (given by the
arrows; see text).

FIG. 4. The single-particle energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Si,
Si10, and Si15 clusters either completely hydrogenated (dashed line) or with
one single-bonded fluorine (solid line) or one double-bonded oxygen (dotted line).

squares) for these clusters as a function of the diameter, \( D \),
defined as \( D = a [ (3/4 \pi) N ]^{1/3} \) where \( N \) is the number of sili-
con atoms and \( a \) is the lattice constant. Figure 3 shows the
optical gap increasing as the size of the cluster is decreasing,
thus demonstrating the key role played by quantum confine-
ment. For clusters smaller than 1.8 nm in diameter, the "oxy-
gen gap," formed by transitions between the states localized
close to the oxygen double bond [see Fig. 2(c)], is smaller
than the gap of the purely hydrogenated clusters. As the clus-
ter size increases beyond this critical 1.8 nm diameter, the
fundamental HOMO-LUMO gap of pure hydrogenated sili-
con nanoclusters decreases below this oxygen gap and the
lowest optical gap is determined by the core transitions.

We also performed QMC calculations on several clusters
terminated completely with hydrogen and those passivated
with a double-bonded oxygen (\( \text{SiH}_2\text{O}, \text{Si}_2\text{H}_2\text{O}, \text{Si}_3\text{H}_1\text{O}, \text{Si}_{10}\text{H}_{14}\text{O}, \text{Si}_{15}\text{H}_{18}\text{O} \), and \( \text{Si}_{30}\text{H}_{32}\text{O} \) to verify that the LDA trends for
passivants other than hydrogen are well reproduced by
QMC. We find in Fig. 3 that the LDA trends in the size
dependence of the optical gap are verified by our QMC cal-
culations. The shift in the gap from LDA to QMC (empty
circles and squares in Fig. 3) in totally hydrogenated clusters
is much greater (around 1.5 eV) than in those with oxygen
contamination (around 0.6 eV). We believe that the difference
in shifts originates from the larger excitonic binding in the
oxygen passivated clusters where the oxygen-derived
HOMO and LUMO states are more localized than in the
absence of such contaminants. Extrapolation of our QMC
calculations (solid line in Fig. 3) suggests that the critical
size beyond which the oxygen gap will no longer be ob-
served is between 2 and 2.5 nm, larger than the 1.8 nm size
predicted by LDA, yet smaller than the 3.0 nm predicted by
empirical tight-binding calculations.20

Although the passivation most drastically affecting the
gap of the clusters appears to be related to double-bonded
passivants, we investigated the possibility that single-bonded
passivants may exhibit a similar effect, and that the states
reduce the gap and that the greater the distortion, the greater the reduction.

V. DIFFERENT OXYGEN TERMINATION STRUCTURES

In addition to replacing two hydrogen atoms from an SiH₂ surface group to form an Si–O double bond, oxygen may also bond with the surface of a silicon nanocluster in either a bridged (Si–O–Si) network or inside the cluster at an interstitial position. In the bridged case, the oxygen atom replaces two hydrogen atoms from two separate Si atoms [see Fig. 6(a)]. Although in principle one could place an oxygen anywhere in the cluster interstitially, we limit ourselves to the lowest energy cases, which for smaller clusters is the bond between a SiH₃ group and the cluster. As SiH₃ terminations are typically higher in energy than SiH₂ and SiH terminations, we only comment on interstitial oxygen in very small clusters where SiH₃ terminations are still present, e.g., Si₁₇H₃₂ and Si₁₇H₃₆.

In Fig. 6 we compare the structures, total energy, and HOMO-LUMO gaps of two different silicon nanoclusters, both with diameters of ~1 nm, with double-bonded and bridged oxygen terminations, Si₂₉H₃₄O and Si₃₅H₃₄O. In Si₂₉H₃₆, the proximity of SiH₂ pairs on a (100)-like facet allows oxygen to replace two hydrogens (Si₂₉H₃₄O) from adjacent SiH₂ groups and to form a bridged bond without significantly distorting the sp³ network [see Fig. 6(a)]. The bond angle between any of the atoms bonded to the silicon and the oxygen is altered by no more than 2° from the initial tetrahedral bonding angle. The resulting LDA single-particle gap is only 0.5 eV lower than the LDA gap in Si₂₉H₃₄ and the QMC gap is also only 0.5 eV lower than the Si₂₉H₃₆ QMC gap. The shift from LDA to QMC is therefore 1.5 eV, not 0.6 eV as in the cluster with a double-bonded oxygen. This particular bridged structure is 2.2 eV lower in energy than the structure with a double-bonded oxygen passivant (as calculated in LDA) due to the smaller strain. In Si₃₅H₃₄O, no such (100) facet exists, and so forming an Si–O–Si bridge alters the ideal bond network significantly, with the resulting bond angles distorted by more than 30° from the original sp³ structure. This distortion causes the bridged configuration to be 2.7 eV higher in energy than the equivalent cluster with a double-bonded oxygen, and the gap decreases by a significantly greater amount, over 1 eV in LDA and almost 3 eV in QMC, thus supporting our earlier claim that any passivation process that significantly distorts the sp³ network will also alter the gap.

In Fig. 7(a) we compare the LDA predicted size dependence of the HOMO-LUMO gap for hydrogenated silicon nanoclusters with those containing a single-oxygen passivant that is double-bonded, bridged, and at an interstitial position. In Fig. 7(b) we plot the size dependence of the difference in total energy between the double-bonded and bridged geometries for the oxygen passivant. Figure 7(a) shows that the nanoclusters completely terminated with hydrogen always have the largest gaps and the corresponding cluster with double-bonded oxygen always has the smallest gap. The predicted gap for the clusters with a bridged oxygen varies from being close to the pure hydrogen gap to close to the double-bonded gap. We observe that for either small clusters in which surface hydrogen atoms are in close proximity (Si₁₂H₂O, Si₁₄H₁₀O, and Si₁₇H₁₄O) or in larger clusters in which a (100) facet exists (Si₂₉H₃₄O and Si₆₆H₆₂O), the bridged oxygen introduces little distortion into the lattice and the bridged geometry is lower in energy than the double-bonded geometry. In these clusters the predicted gaps of the clusters containing a bridged oxygen are significantly larger than those of the clusters containing a double-bonded oxygen. Conversely, for Si₁₅H₃₂O and Si₁₅H₇₄O where the bridged structure introduces significant geometric distortion, the energy is higher than the cluster with the double-bonded geometry and the predicted gap is almost as low. For the few cases where we calculated a cluster with an oxygen interstitially placed, we predict relatively large optical gaps, falling very close to the maximum (fully hydrogenated) gap.
ever, in cases where no SiH₃ termination exists, the gap of a cluster with an interstitial oxygen could be significantly smaller due to distortion placed in the lattice. In order to make connection to recent experiments, we have performed QMC calculations on many of these silicon nanoclusters with oxygen occurring in multiple geometries. We find that the QMC optical gap of clusters containing double-bonded oxygen is about 0.6 eV higher than the LDA gap and that a significant deviation between the double-bonded cluster gap and the other geometries gaps exists.

These results are in contradiction to published time-dependent LDA (TD-LDA) results in which oxygen occurring in different geometries on the same size cluster had very similar gaps, significantly higher than our QMC gaps. We believe that this higher definition of the optical gap is due to the chosen threshold of 10⁻⁴ used to define the optical gap at the absorption edge. We have repeated these TD-LDA calculations defining the first nonzero matrix element as the onset of the optical gap. Using this definition, which we believe is more appropriate for comparison with QMC and LDA gaps, we find TD-LDA absorption gaps which exhibit a negligible shift from the original LDA gap and that do indeed show a substantial difference in gaps of clusters with oxygen attached in different geometries [Fig. 7(a)].

VI. EFFECT OF MULTIPLE OXYGEN TERMINATION

In Fig. 8 we compare our QMC predictions for the size dependence of the optical gap of silicon nanoclusters terminated with pure hydrogen and those with a single double-bonded oxygen atom to recent experiments in which oxygen was present. The optical gap predicted by our QMC calculations for clusters passivated with a single oxygen double bonded to the surface is too large compared with this experimental data. In addition to the problem of wide experimental size distribution, a number of other reasons for this discrepancy are possible. First, the nanoclusters used in various experiments are not guaranteed to be crystalline as assumed in our calculations. Transmission electron microscopy images of very small clusters may be misleading as electron beams can actually anneal the nanoclusters causing a previous noncrystalline structure to crystallize. Therefore, the measured absorption and emission gaps may possibly be taken from amorphous silicon. Second, surface reconstruction, including silicon dimers, are known to cause a gap reduction and silicon clusters may not only be contaminated with oxygen, but also consist of a series of dimerized, reconstructed surfaces. Finally, the effect of multiple-oxygen passivation should be considered. Our discussion so far has only considered the effect on the optical gap of a single-oxygen passivant (contaminant). It is interesting to consider whether the strain introduced by the presence of a single-oxygen passivant is likely to deter the bonding of additional oxygen passivants, and if so, how will these multiple oxygens affect the gap.

On the spherical Si₆₆ cluster there are 24 possible sites where an oxygen atom could form a double bond with a surface atom, and 12 aligned dihydrides where it is possible to add bridged oxygen atoms in its lowest energy structure. In order to test the stability of Si₆₆H₆₄–₂₆O, we calculated the energetic cost of adding successive double-bonded or
bridged oxygen atoms. We first calculated the total energy difference of the clusters $\text{Si}_{6\alpha}$H$_{64}$ and $\text{Si}_{6\sigma}$H$_{6\sigma}$O where the oxygen atom is double bonded to any of the 24 possible sites. Each site is symmetrically equivalent and so this energy difference is independent of the choice of site. We then calculated the total energy difference between the clusters $\text{Si}_{6\alpha}$H$_{6\alpha}$O and $\text{Si}_{6\sigma}$H$_{6\sigma}$O$_{2}$, where the second oxygen atom was placed either alongside the first oxygen [Fig. 9(a)], replacing successive pairs of dihydrides [Fig. 9(b)] or on the opposite side of the cluster [Fig. 9(c)]. The energy differences associated with adding the second oxygen atom varied by $<0.2$ eV among all 23 possible sites. In addition, the energy differences associated with adding the second oxygen atom were within $<0.1$ eV of that for adding the first oxygen, and this difference remained constant up to the final (24th) oxygen atom; i.e., it is just as favorable to add the first oxygen as it is to add the 24th. Similar calculations for the addition of oxygen in bridged positions [Fig. 9(d)] yielded similar results. We therefore predict that from purely thermodynamic arguments, if the chemical potentials of hydrogen and oxygen is such that it is favorable to replace two surface hydrogen atoms with an oxygen, the oxygenation reaction is likely to continue replacing additional hydrogens with oxygen. Little “repulsion” is present, either due to strain or due to electrostatic interactions between the oxygen atoms on the surface of the cluster.

Figure 10 shows the predicted LDA HOMO–LUMO gap of $\text{Si}_{6\alpha}$H$_{64}$–$2\alpha$O$_{2}$ clusters as a function of oxygen coverage. Unlike $\text{Si}_{35}$H$_{6\alpha}$–$2\alpha$O$_{2}$, and $\text{Si}_{3\sigma}$H$_{6\sigma}$–$2\alpha$O$_{2}$, these clusters have dihydrides aligned next to each other, similar to a silicon (100) surface. The solid circles show the predicted gaps for these clusters with double-bonded oxygen atoms while the solid squares show predicted gaps for clusters with bridged oxygen atoms. All 24 double-bonded sites are symmetrically equivalent and hence, when only one oxygen atom is double bonded to the surface, the optical gap is unique. When two oxygen atoms are double bonded to the cluster, the relative locations of the oxygen atoms has a small effect on the strain induced in the cluster and the value of the gap is particularly sensitive to this small amount of strain. The error bars shown for the predicted gaps of clusters with 2, 3, and 4 oxygen atoms show the dependence of HOMO–LUMO gap on the relative locations of the oxygen passivants. When two oxygen atoms terminate the surface, the largest gap occurs when the two oxygens are on opposite sides of the cluster [Fig. 9(c)] and the smallest gap occurs when the two oxygens are on neighboring dimers [Fig. 9(a)]. The solid squares in Fig. 10 show the predicted gaps for clusters with bridged oxygen terminations. The gaps of $\text{Si}_{6\sigma}$ clusters with bridged oxygen terminations are significantly larger than the gaps of $\text{Si}_{6\alpha}$ clusters with oxygen in double-bonded positions.

By shifting our QMC predicted optical gaps according to the effects of multiple oxygen passivation predicted within LDA, we compare in Fig. 8 these predictions with those experiments in which particles were synthesized in the presence of oxygen. The wide range of possible gaps that may be obtained when oxygen contaminates the surface can perhaps explain the wide discrepancy between so many experiments in which either oxygen was present, or the impurities were unknown.

The dipole oscillator strengths associated with the absorption of a photon in the cluster and the lowest observed transitions also vary with multiple oxygen passivation. When six oxygen contaminate the surface of a $\text{Si}_{35}$ cluster, we obtain allowed dipole transitions that occur much lower than those with a single oxygen. The lowest observed transition occurs at 0.6 eV lower than the smallest unobserved transition in a single double-bonded oxygen cluster. These LDA estimates of oscillator strengths were verified by independent TD-LDA results, and show that such transitions will be observed experimentally.

**VII. CONCLUSION**

In conclusion, we have demonstrated that quantum confinement is just one mechanism responsible for optical tran-
sitions in silicon nanoclusters and that the specific surface chemistry must be considered to interpret experimental results. We have carried out an analysis of the densities associated with the HOMO and the LUMO of silicon nanoclusters passivated with hydrogen up to 1.8 nm in diameter as well as Si_{15}H_{18}X and Si_{13}H_{34}Y where X=H, F, Cl, or OH and Y=O, S, or CH_2. Our calculations show that surface effects due to the different chemistry of single-bonded passivants do not appreciably contribute to optical transitions, even in the case of highly electronegative passivants, although the strength of the transition may be larger. In systems with double bonds (e.g., O as a passivant), we demonstrate that the local distortion of the sp^3 network at the surface significantly affects the energy of photoluminescence. Disruption of the sp^3 network induced by double-bonded passivants closes the single-particle gap by at least 1 eV in the LDA and the QMC calculated optical gap by 2 eV for clusters 1 nm in diameter. Our results show that a range of absorption gaps could be seen using passivants such as O, S, and CH_2 and that even a single contaminant can have a large impact on experimental results. We also discovered that multiple contaminants can further alter the gap giving a large range of observed results, perhaps partially accounting for wide discrepancies in experiments. We found that bridged oxygen may also alter the gap, especially if it distorts the network significantly as in Si_{15}H_{34}O, and is not always the most favorable, lowest energy structure.

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29. A. Giannozzi (private communication).
39. M. Rohlfling (private communication).
41. J. Y. Raty (private communication).