

## Surface Chemistry of Silicon Nanoclusters

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We employ density functional and quantum Monte Carlo calculations to show that significant changes occur in the gap of fully hydrogenated nanoclusters when the surface contains passivants other than hydrogen, in particular atomic oxygen. In the case of oxygen, the gap reduction computed as a function of the nanocluster size provides a consistent interpretation of several recent experiments. Furthermore, we predict that other double bonded groups also significantly affect the optical gap, while single bonded groups have a minimal influence.

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Reducing the size of a semiconductor to the nanometer scale changes the physical properties of the material in a fundamental way. For example, semiconductor clusters with a diameter of a few nanometers exhibit an increased optical gap and narrower emission spectra compared to bulk values [1]. In addition, reducing the size to the nanometer scale causes a dramatic increase of surface area to volume ratio; therefore, the physical and chemical properties of semiconductor nanoclusters are greatly influenced by surface reconstruction, passivation, and ultimately by surface chemistry.

To date, most of the experimental work designed to exploit the unique optical properties of semiconductor nanoclusters has focused on II/VI semiconductors such as CdSe, CdS, and CdTe [2,3] as these particles are easier to synthesize with narrow size distributions and well passivated surfaces than III/V and group IV nanoclusters. Although the effect of surface reconstructions and surface chemistry on II/VI compounds has not been studied in detail, that quantum confinement dominates the optical properties of these systems is generally accepted [2,3]. In contrast, silicon nanostructures are much less well characterized and the interplay of quantum confinement effects and surface properties is still unclear.

Silicon offers technical advantages over the CdSe class of nanostructures for a number of applications, such as silicon nanocluster lasers and as a biologically compatible substitute for fluorescent dyes. Despite investigations of Si nanoclusters [4–8] and of the related topic of porous Si [9,10], basic problems related to the physics of photoluminescence (PL) remain unsolved. In particular, few surface sensitive probes for nanoclusters are available and experimentally distinguishing bulk from surface effects is difficult. In addition, theoretical modeling [11–15] is particularly challenging in the few nanometer size regime, as a full quantum mechanical description of both core and surface properties of the nanoclusters is required to provide accurate and predictive data.

Recent studies on the role of surface chemistry on the optical properties of silicon nanoclusters have reported conflicting levels of importance, ranging from minimal [6,8,16,17] to crucial [5,7,10]. In particular, experiments

investigating the effect of oxygen in both porous silicon [10] and hydrogen passivated nanoclusters [7,8,16] have generated conflicting results. Oxygen exists in many experiments as a contaminant [6,16] and may also be intentionally used to saturate dangling bonds [5,7,10]. Discrepancies between experiments have arisen both with respect to the shift in the emission spectra and the changes in intensity when oxygen is adsorbed onto hydrogenated silicon nanoclusters. With the exception of oxygen, very few detailed experimental studies of surface passivants have been undertaken and no calculations, beyond small molecules [17,18], have been reported to date.

In this Letter, we present the first *ab initio* investigations of the effect of surface passivants on the optical gap of Si nanoclusters with diameters up to  $\approx 2$  nm. We carry out first-principles calculations using both density functional theory (DFT) and quantum Monte Carlo (QMC) techniques. Our results show that below 2–2.5 nm, atomic oxygen double bonded to surface Si atoms causes a significant closing of the gap with respect to that of hydrogen saturated nanoclusters. These findings provide a consistent interpretation of several recent experiments [5–7]. Our calculations show that the effect of double bonded passivants such as sulfur and  $\text{CH}_2$  is similar to that of oxygen, whereas the effect on the gap of single bonded passivants such as a hydroxyl group and atomic F and Cl is negligible.

Our DFT calculations were based on the local density approximation (LDA) and the generalized gradient approximation (GGA) using a pseudopotential plane wave approach [19]. The initial geometries for spherical H-passivated clusters were constructed using a diamond structure core with bulk Si-Si bond lengths, surface atoms having one or two dangling bonds. Hydrogen was then placed along the appropriate tetrahedral direction at a reasonable distance (i.e., the Si-H distance in  $\text{SiH}_4$ ). Single (double) bonded passivants were placed on silicon atoms replacing one (two) hydrogen(s). We adopted the Si=O double bonded structures proposed in Ref. [10] which we find to have lower energy than bridged Si-O-Si structures for Si clusters with a 35 atom core. All the initial structures were then relaxed until the residual forces were less than  $2 \times 10^{-4}$  eV/Å. The changes with

respect to the initial geometries were in general small. For example, in  $\text{Si}_{35}\text{H}_{36}$  the relaxed Si-Si bond lengths were 0.7% smaller than in bulk while the Si-H bonds at the surface increased from the bond length in  $\text{SiH}_4$  by 2.0%. GGA calculations using the PBE exchange-correlation functional [22] yielded nearly identical highest occupied molecular orbital(HOMO)–lowest unoccupied molecular orbital(LUMO) gaps compared with the LDA.

After performing DFT geometry optimizations and HOMO-LUMO gap calculations, QMC calculations were carried out to verify that the DFT trends for the HOMO-LUMO gap as a function of size and surface chemistry are predictive. In particular, we performed QMC calculations [23–25] for the optical gap  $\epsilon^{\text{opt}} = E_N^* - E_N$ , where  $E_N$  ( $E_N^*$ ) is the total energy of the cluster in its ground (excited) state, for  $\text{Si}_{10}\text{H}_{16}$ ,  $\text{Si}_{10}\text{H}_{14}\text{O}$ ,  $\text{Si}_{35}\text{H}_{36}$ , and  $\text{Si}_{35}\text{H}_{34}\text{O}$ . These QMC calculations represent the largest calculations to date on hydrogenated silicon clusters and were made possible by a recent development in the QMC approach [25].

Figure 1(a) shows our calculated LDA HOMO-LUMO gaps and lowest QMC optical gaps of H-passivated silicon nanoclusters with and without oxygen, as a function of cluster size. Our LDA results for fully hydrogenated nanoclusters show good agreement with previously published DFT values [13,26], and our QMC results on small clusters agree with those of accurate GW calculations [15]. For fully hydrogenated nanoclusters, the LDA gaps track the QMC gaps, but LDA values are shifted approximately 1.5 eV lower [27]. The LDA gaps of the oxygen passivated clusters also track the QMC gaps but with a smaller 0.6 eV shift. This smaller shift may arise from a stronger electron-hole binding energy, due to the more localized oxygen-like states (see Fig. 2). Overall, the LDA gap trends as a function of size for both pure hydrogen and mixed hydrogen/oxygen passivated clusters are well reproduced by our QMC calculations.

For the oxygen-contaminated clusters smaller than 2–2.5 nm, we find that the HOMO and the LUMO states are localized in the vicinity of the Si=O double bond [28] (see Fig. 2). In Fig. 1(a), the size range where we expect surface oxygen and core silicon states to cross is marked with arrows. These results are in qualitative agreement with those of Wolkin *et al.* [10], although those semiempirical tight binding calculations predicted that oxygen states should disappear from the gap above 3 nm instead of 2–2.5 nm.

In Fig. 1(b) we compare our findings with three recent measurements of the gaps of oxygen passivated silicon nanoclusters [5–7]. The solid red curves in Fig. 1(b) replot our QMC results from Fig. 1(a). The dashed red line marks an approximate QMC gap for multiply oxygenated clusters (estimated from LDA calculations, assuming that the QMC reduction of the gap is similar to the LDA reduction). Increasing the oxygen concentration at the surface reduces the value of the LDA gap by approximately 0.6 eV with

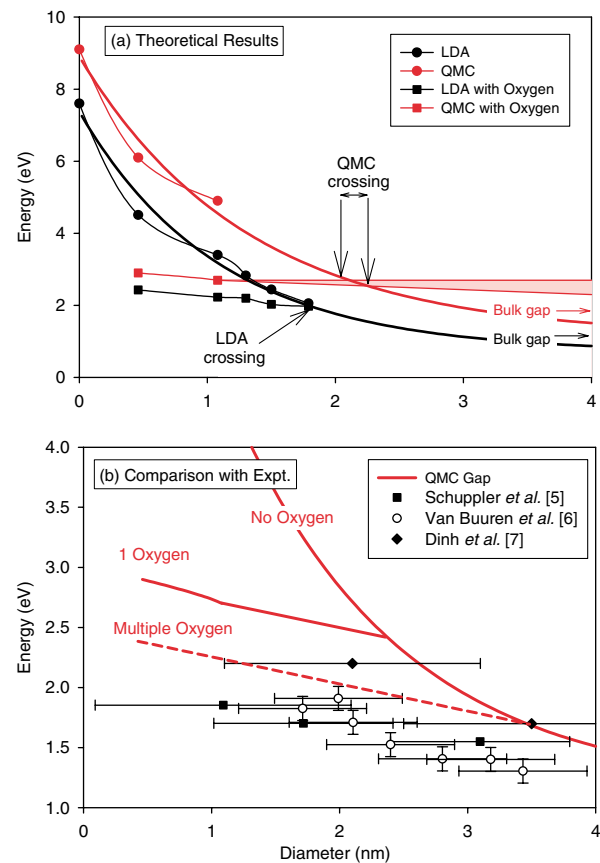


FIG. 1 (color). Energy gap versus diameter (nm) for hydrogen passivated silicon nanoclusters with and without oxygen. The upper panel (a) shows results of LDA (black) and QMC (red) calculations. All QMC statistical error bars are smaller than the symbols. The calculated gaps of the fully hydrogenated clusters are marked by filled circles. The thick red and black curves are exponential fits to these calculated gaps that approach the respective bulk silicon gaps. The calculated gaps for clusters with one double bonded oxygen substituted for two hydrogens are marked by filled squares and are extrapolated into the red shaded region. The lower panel (b) compares the results of recent experiments with the above (solid) curves fitted to the QMC gaps for hydrogenated and oxygen passivated clusters. An additional curve (dashed line) shows the predicted QMC gap for multiple oxygen passivated clusters (see text).

respect to the single oxygen case. We note that the measurements in Refs. [6] and [8] on oxidized clusters have been interpreted as showing that quantum confinement is the only mechanism responsible for PL, regardless of the passivating surface. Our calculations clearly show (i) that pure quantum confinement effects produce a much larger gap (3–4 eV) as a function of size in the 1–2 nm range, in agreement with Refs. [11–15], and (ii) that a better agreement with experiment can be obtained when the presence of multiple oxygen atoms at the surface is taken into account. A more detailed investigation on oxygen coverage will be discussed elsewhere [30].

In order to analyze the physical origin of the effect of oxygen on the gap, we investigated the effect of other contaminants on the energy gap. In particular, we investigated

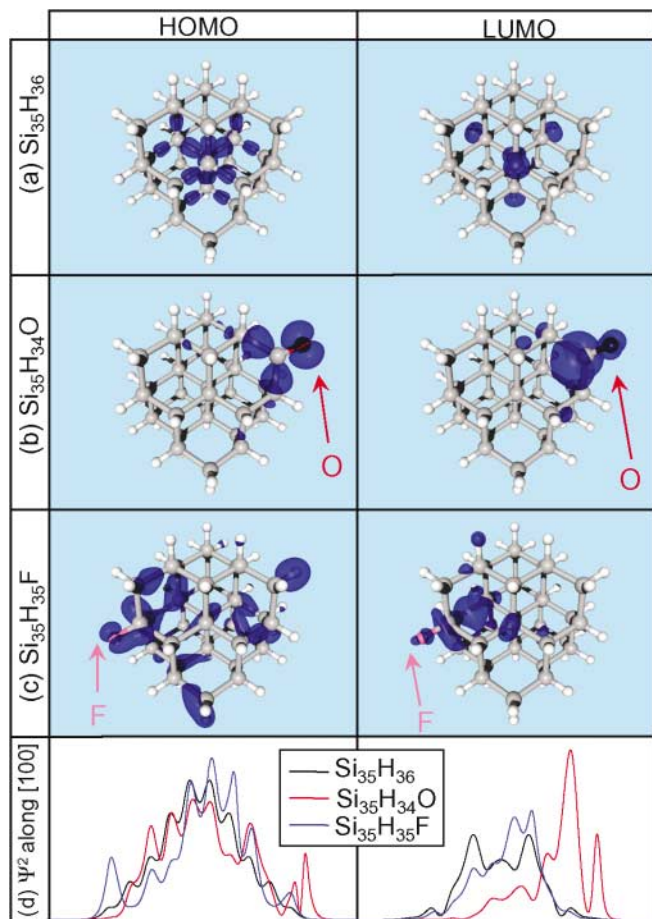


FIG. 2 (color). Isosurfaces of the square modulus of the highest occupied and lowest unoccupied Kohn-Sham orbitals of  $\text{Si}_{35}\text{H}_{36}$ ,  $\text{Si}_{35}\text{H}_{34}\text{O}$ , and  $\text{Si}_{35}\text{H}_{35}\text{F}$ . Panel (a) shows charge density isosurfaces plotted at 50% of the maximum amplitude of the HOMO and LUMO orbitals in  $\text{Si}_{35}\text{H}_{36}$ . Panels (b) and (c) show charge density isosurfaces plotted at 10% of their respective maximums. Panel (d) shows the average HOMO and LUMO charge density in a series of  $\{100\}$  planes along the  $[100]$  direction.

whether the gap closing is related to the high electronegativity of the contaminant, the electronic levels of the passivant such as the lone pair state appearing in the middle of the gap, or the chemical environment, specifically, the existence of a double bond.

Oxygen is highly electronegative (3.5), comparable to fluorine and chlorine. To test the effect of the electronegativity of the passivants, we calculated the gaps of  $\text{Si}_{35}\text{H}_{35}\text{F}$  and  $\text{Si}_{35}\text{H}_{35}\text{Cl}$ . A comparison of the molecular energy levels for each of these clusters (see Fig. 3) reveals that F and Cl have relatively little effect on the gap, although the energy of the LUMO decreases slightly with respect to the fully hydrogenated cluster. The principal effect of these passivants is to break the  $T_d$  symmetry and split the three degenerate HOMO states.

To further analyze whether there is some other characteristic of oxygen accounting for its closing the gap, such as the lone pair state of oxygen, we passivated  $\text{Si}_{35}\text{H}_{35}$

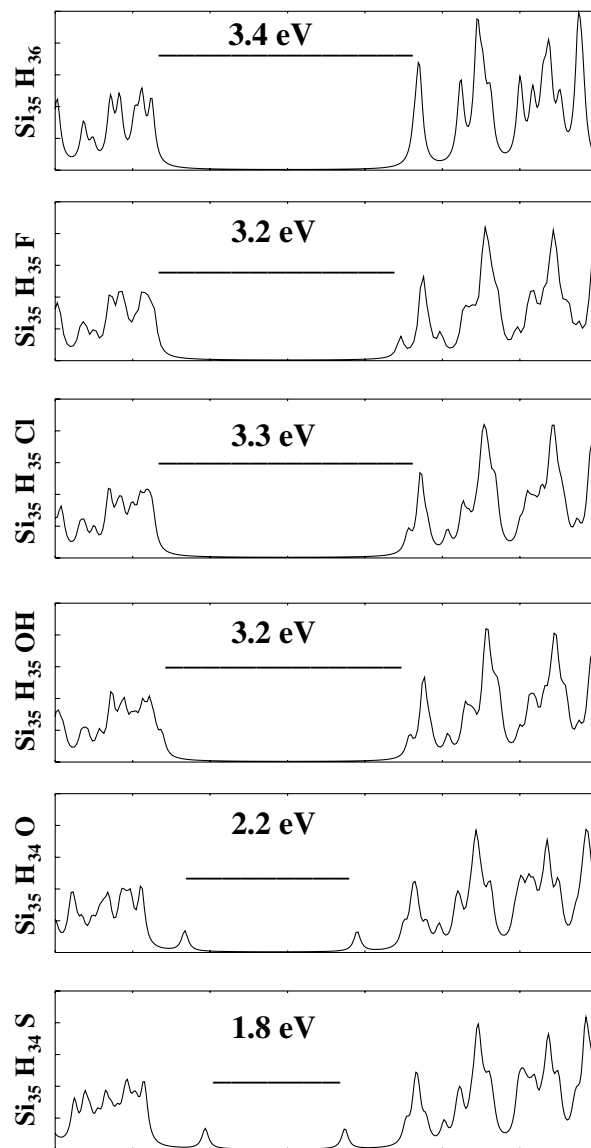


FIG. 3. LDA calculated density of states (Lorentzian broadened) of a  $\text{Si}_{35}\text{H}_{36}$  cluster passivated with F, Cl, OH, O, and S groups. The single particle gaps are marked by the horizontal bar.

with OH, which has a lone pair, and  $\text{Si}_{35}\text{H}_{34}$  with  $\text{CH}_2$ , a passivant with no lone pair. In the OH case, we observe a slight decrease in the gap from the H-passivated silicon value, similar to the effect of the other single bonded elements (F and Cl). In the  $\text{CH}_2$  case we found instead a large reduction of the gap, similar to atomic oxygen, yet there is no lone pair in the  $\text{CH}_2$  group. It appears, therefore, that neither the electronegativity of oxygen, nor its lone pair state is responsible for the significant gap closing. However, much as with oxygen and  $\text{CH}_2$ , a large closing of the LDA gap from 3.4 to 1.8 eV occurs when a double bonded sulfur atom is used to passivate the surface. Similar to oxygen, the HOMO and LUMO are localized on the passivant.

Figure 3 summarizes our LDA results for all the passivants considered here. The molecular energy levels of

$\text{Si}_{35}\text{H}_{35}\text{X}$  where  $X = \text{H}, \text{OH}, \text{Cl},$  and  $\text{F}$  are nearly identical, with a 0.1 to 0.2 eV variation on the gap. Likewise, the three passivants forming double bonds with the surface (O, S, and  $\text{CH}_2$ ), have similar energy levels (very different from the single bonded passivants). The small, systematic shifts in the LUMO of the nanoclusters with a single bonded passivant (F,Cl,OH) replacing an H suggests that as long as silicon remains in its favorable  $sp^3$  network, the core states will be only slightly altered. However, when a double bonded passivant (O, S, or  $\text{CH}_2$ ) is added to the nanocluster, the  $sp^3$  network is considerably distorted and the HOMO and LUMO change their nature significantly (see Fig. 2). The distortion induced by sulfur on its surrounding network is bigger than that of oxygen, possibly accounting for the additional reduction in the gap.

In conclusion, we have demonstrated that quantum confined core states represent just one mechanism responsible for the observed optical gap in silicon nanoclusters and that the specific surface chemistry must be taken into account in order to quantitatively explain the optical properties of these systems. Our results indicate that a range of absorption gaps could be seen using different passivants and that one contaminant can have a large impact on the measured value of the optical gap. We carried out an analysis of densities associated with the HOMO and LUMO states for silicon nanoclusters passivated with hydrogen up to 1.8 nm in diameter as well as  $\text{Si}_{35}\text{H}_{35}\text{X}$  and  $\text{Si}_{35}\text{H}_{34}\text{Y}$  species where  $X = \text{H}, \text{F}, \text{Cl},$  or  $\text{OH}$  and  $Y = \text{O}, \text{S},$  or  $\text{CH}_2$ . Our calculations show that surface effects due to single bonded passivants make a small contribution to optical transitions, even in the case of highly electronegative atoms. For double bonded passivants, e.g., O, we showed that the gap is reduced by at least 1 eV for clusters 1 nm in diameter. This reduction is accompanied by a sizable local distortion of the  $sp^3$  network at the surface. We interpret the wide discrepancy between previous theoretical data [11,12,14] and experimental results [5–7] to be due to multiple oxygen contamination. One possible proposed verification of our results is to expose a silicon cluster ( $<2$  nm) to sulfur, while care is taken not to expose it to oxygen. We predict that such a cluster will exhibit a similar red shift as those clusters exposed to oxygen, thus demonstrating the importance of double bonded passivants to the optical properties of silicon nanoclusters.

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[27] In this narrow size regime it appears that the size dependence of the electron-hole binding energy and self-energy corrections to the LDA single particle gap partially cancel, leaving a size independent (1.5 eV) correction.

[28] Note, in this case DFT and GW-BSE calculations [29] indicate that the HOMO to LUMO transition is weak and may not be observed in absorption experiments. Our calculations show that the HOMO-1 to LUMO transition has a strong dipole matrix element and lies  $\sim 0.2$  eV higher in energy.

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