# Excitons in silicon nanocrystallites: The nature of luminescence

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The absorption and emission spectra of silicon nanocrystals up to 1 nm diameter have been calculated within a first-principles framework. Our calculations include geometry optimization and the many-body effects induced by the creation of an electron-hole pair. Starting from hydrogenated silicon clusters of different sizes, different Si/O bondings at the cluster surface have been considered. We found that the presence of a Si—O—Si bridge bond causes significant excitonic luminescence features in the visible range that are in fair agreement with experiment.

PACS number(s): 78.67.Bf, 68.65.Hb, 71.35.Cc

Following the initial impulse given by the discovery of photoluminescence (PL) from porous silicon,[1] nanostructured silicon has received extensive attention.[2,3] This activity is mainly focused on the possibility of getting relevant optoelectronic properties from Si nanocrystals (Si-nc). Optical gain, observed in Si-nc embedded in $SiO_2$, has given further impulse to these studies.[4] It is generally accepted that the quantum confinement (QC), caused by the nanometric size, is essential for the PL in Si-nc, but the interpretation of the PL features, such as the substantial redshift (RS) of the PL energy with respect to the theoretical predictions based merely on the QC model and its independence from the size for small ($<3$ nm) crystallites, is still controversial. Baierle *et al.*[5] and G. Allan *et al.*[6] stressed the importance of bond distortion at the Si-nc surface in the excited state (ES) in creating an intrinsic localized state responsible for the PL emission. Wolkin *et al.*[7] observed that also oxidation introduces states in the gap, which pin the transition energies. They and others[8,9] suggest that the formation of a Si=O double bond is responsible for the RS of the optical absorption edge upon oxidation. On the contrary, Vasiliev *et al.*[10] showed that similar absorption gaps can be obtained also for O connecting two Si atoms (bridge bond) at the Si-nc surface. Recently Gatti and Onida[11] considered six small different prototypical oxidized Si clusters and found results similar to those of Refs. 8 and 9—i.e., that the RS of the absorption edge is much more pronounced in the case of the double Si=O bond than for bridge bonds. Ramos *et al.*[12] have found a blueshift of the absorption onset for strongly oxidized Si-nc. Actually, heavy oxidation (the formation of complete oxide shells) originates a reduction of the effective size of the Si-nc—i.e., an increase of QC. Although all these calculations address only the problem of absorption, yet the large majority of experimental results and the most interesting ones are relative to PL measurements and thus are strictly related to excited-state results. To date very few papers have addressed the issue of ES configurations, which is mostly relevant for Si-nc with a high surface-to-volume ratio. Theoretically their description has been performed using the so called ΔSCF method,[13–16] where total energies are calculated both in the ground state (g.s.) and excited state (ES). Here the ES corresponds to the electronic configuration in which the highest occupied single-particle state [highest occupied molecular orbital (HOMO)] contains a hole ($h$), while the lowest unoccupied single-particle state [lowest unoccupied molecular orbital (LUMO)] contains the corresponding electron ($e$). Thus, one can extract the absorption and emission energies and through their difference calculate the Stokes or Frank-Condon shift due to the lattice relaxation induced by the electronic excitation. The obtained results show a dependence of the Stokes shift (SS) on the Si-nc size, which is less marked for the O double-bonded case.

Our aim, here, is to allow a direct comparison between experimental data and theoretical results; thus, we calculate not only the transition energies but also directly the absorption and emission optical spectra. For both the g.s. and ES optimized geometry, we have evaluated the optical response $\text{Im}[\varepsilon_{NC}(\omega)]$ (the imaginary part of the nanocrystal dielectric function) through first-principles calculations also beyond the one-particle approach. We consider the self-energy corrections[17] by means of the *GW* method and the excitonic effects through the solution of the Bethe-Salpeter (BS) equation.[18] The effect of the local fields (LF's) is also included, to take into account the inhomogeneity of the systems.[20] In this work, the emission spectrum has been calculated, in a first approximation, as the time reversal of the absorption.[19] Strictly speaking, $\text{Im}[\varepsilon_{NC}(\omega)]$ corresponds to an absorption spectrum in a structural geometry, the ES ge-

ometry, with the electronic configuration of the g.s. The electron-hole interaction is here considered also in the emission geometry. This different approach, where the many-body effects are combined with the study of the structural bond distortion at the Si-nc surface in the ES, accounts for both the observed absorption and PL spectra. The procedure is exemplified for a small $Si_{10}H_{16}$ (0.55 nm diameter) and a larger $Si_{29}H_{36}$ (0.9 nm diameter) cluster. We demonstrate that light emission in the near-visible range is related to the presence at the Si-nc surface of Si—O—Si surface bridge bonds. Actually we find that a strong excitonic peak at about 1.5 eV emission energy is obtained in the $Si_{10}H_{16}$ cluster with a Si—O—Si bridge bond as a result of a considerable bond distortion affecting the electron-hole interaction. The emission corresponding to the Si=O double bond, on the contrary, is predicted to occur at a much larger energy as a consequence of a much smaller structural distortion and of a first electronic transition almost dark. Similar results have been obtained for the larger $Si_{29}H_{36}$ cluster.

For all clusters the starting configuration is the hydrogenated surface ($Si_{10}H_{16}$ and $Si_{29}H_{36}$). Two types of Si/O bonds, the silanone-like Si=O bond ($Si_{10}H_{14}$=O and $Si_{29}H_{34}$=O) and the Si—O—Si bridge bond, where the O atom is in between two Si atoms as in the $SiO_2$ ($Si_{10}H_{14}$>O and $Si_{29}H_{34}$>O), are then substituted into the H—Si surface bonds. It is worth noting that the bridge bond we consider has been demonstrated to lead to the stablest isomer configuration by Gatti and Onida.[11,21] Full relaxation with respect to the atomic positions is performed within the density functional theory (DFT) limit for all systems in both the ground and excited configurations using norm-conserving local density approximation (LDA) pseudopotential with an energy cutoff of 60 Ry.[22] Figure 1 presents the relaxed optimized structures of the considered $Si_{10}$-based clusters in their electronic g.s. and ES configurations. The ionic relaxation has produced structural changes with respect to the initial geometry which strongly depend on the type of surface termination.

In $Si_{10}H_{16}$, some atomic distortion occurs at the surface in the excited-state more than in the ground-state geometry and the Si—Si distances in the core shells are somewhat altered by the excitation. In the case of $Si_{10}H_{14}$=O, the changes are mainly localized near the O atom; in particular, the angle between the double-bonded O and its linked Si atom is modified (see Fig. 1). In the bridge structure ($Si_{10}H_{14}$>O), instead, the deformation is localized around the Si—O—Si bond determining a considerable strain in the Si—Si dimer distances.[21] Similar results are obtained for the larger $Si_{29}$-based clusters. The only difference is that now the distortion induced by the promotion of an electron is smaller, as expected, since for larger clusters the charge density perturbation is distributed throughout the structure and the effect locally induced becomes less evident.

These structural changes are reflected in the electronic and optical properties. This is shown in Table I, where the calculated optical gaps (energy differences between the LUMO and HOMO) at different levels of approximation are reported for both the $Si_{10}$- and $Si_{29}$-based nanocrystals. The main result common to absorption and emission is the opening of the LDA band gap with the $GW$ corrections by
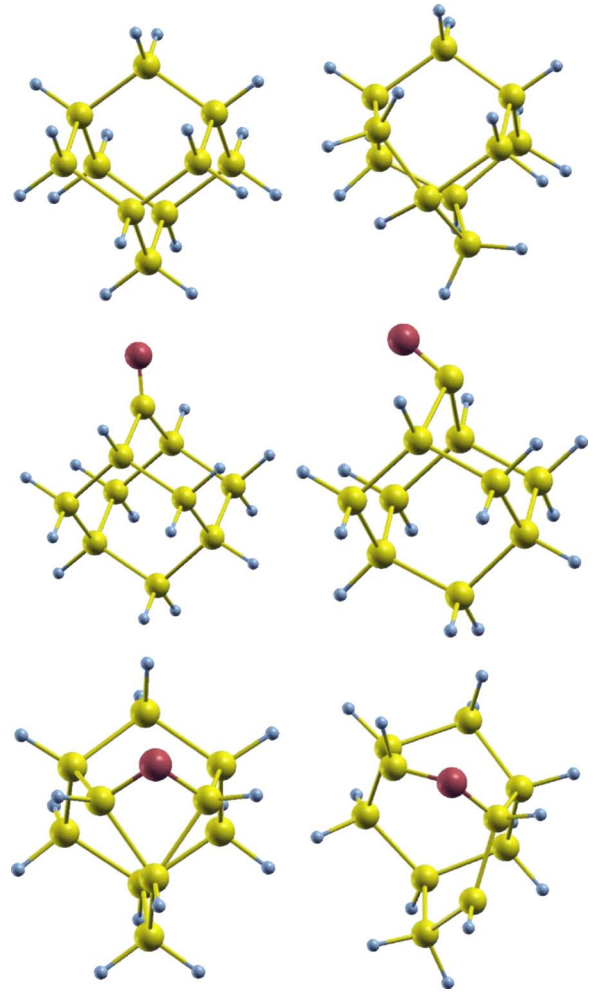


FIG. 1. (Color online) Calculated structures for the $Si_{10}H_{16}$ (top panel), $Si_{10}H_{14}$=O (central panel), and $Si_{10}H_{14}$>O (bottom panel) clusters at relaxed geometry in both the ground (left panels) and excited (right panels states). Gray (yellow) balls represent Si atoms, and the black (red) ball is the O atom, while the small gray (gray) balls are the hydrogens used to saturate the dangling bonds.

amounts weakly dependent on the surface termination but much larger than the corresponding 0.6 eV of the Si bulk case. Looking at the BS-LF calculations, we note a sort of compensation (more evident in the g.s. than in the ES) of the self-energy and excitonic contributions: the BS-LF values

TABLE I. Absorption and emission optical gaps calculated within DFT-LDA, $GW$, and with the inclusion of excitonic and local field effects (BS-LF). In parentheses also the lowest dark transitions (when present) are given. All values are in eV.

| | Absorption LDA $GW$ BS-LF | Emission LDA $GW$ BS-LF |
|---|---|---|
| $Si_{10}H_{16}$ | 4.6, 8.6, 5.2 | 0.1, 3.8, 0.4 |
| $Si_{10}H_{14}$=O | 3.3 (2.5), 7.3 (6.5), 3.7 (2.7) | 0.8, 4.6, 1.0 |
| $Si_{10}H_{14}$>O | 3.4, 7.6, 4.0 | 0.1, 3.5, 1.5 |
| $Si_{29}H_{34}$=O | 2.5, 6.0, 3.7 (3.1) | 0.9, 4.1, 1.2 |
| $Si_{29}H_{34}$>O | 2.3, 4.8, 2.3 | 0.4, 3.0, 2.2 (0.3) |

return similar to the LDA ones. This compensation has been predicted theoretically by Delerue *et al.*[23] in zero-dimensional nanomaterials. The only exceptions are the BS-LF calculations for the excited-state geometries of the clusters with Si—O—Si bridge bonds at the surface.

Concerning the absolute values of all the absorption and emission gaps it is worthwhile to note that whereas absorption predicts the correct trend as a function of size (i.e., larger gap for smaller Si-nc), this is not the case for emission, where the situation is more complex. This is due to the significant cluster distortion in the ES of the smaller Si-nc. Here the Stokes shift is so strong that the emission energies are now smaller for the smaller cluster.[24] The fact has been previously discussed for the case of fully hydrogenated Si-nc, where, by total energy calculations,[14–16] it has been demonstrated that the usual trend is recovered also for the emission when the Si-nc have a diameter $\geq$1 nm. From the absorption and emission gaps, we can now estimate the Stokes shift fully including the excitonic effects (the BS-LF results). In the case of $Si_{10}$-based clusters, the fully hydrogenated ones show a remarkable Stokes shift (4.8 eV) as a consequence of the excitation whereas the double-bonded O clusters and the bridge-bonded O clusters present practically the same shift (2.7 eV and 2.5 eV). These last shifts become, in the case of the $Si_{29}$-based clusters, 2.5 eV and 0.1 eV, respectively. It should be noted that if the SS's were calculated simply as differences of emission and absorption energies of the lowest transitions (without looking at the oscillator strength—i.e., without considering if these transitions are dark or not) for the $Si_{10}H_{14}$=O cluster, we would obtain a weaker SS (1.7 eV) and for the $Si_{29}H_{34}$>O cluster a stronger SS (2.0 eV).[24] A clearer insight into these results is offered by Fig. 2, where the calculated absorption and emission spectra for all the $Si_{10}$-based clusters are depicted. Self-energy, local-field, and excitonic effects (BS-LF) are fully taken into account. Concerning the absorption spectra (Fig. 2, dashed lines), all three cases show a similar smooth increase in the absorption features. Different is the situation for the emission-related spectra (Fig. 2, solid lines). Here, whereas the situation remains similar for the fully hydrogenated $Si_{10}H_{16}$ (top panel) cluster and for the $Si_{10}H_{14}$=O (central panel) cluster, in the case of a Si—O—Si bridge bond (Fig. 2, bottom panel) an important excitonic peak, separated from the rest of the spectrum, is evident at 1.5 eV. Actually bound excitons are present also in the fully hydrogenated (at 0.4 eV) and in the $Si_{10}H_{14}$=O (at 1.0 eV) clusters, with calculated binding energies (the energy difference between the *GW* and BS-LF results) even larger than in the case of the Si—O—Si bridge bond (3.4 and 3.6 eV, respectively, to be compared with a binding energy of 2.0 eV in the case of the bridge bond cluster). Nevertheless, the related transitions are almost dark and the emission intensity is very low. Only in the case of the Si—O—Si bridge bond does a clear PL peak appear thanks to the strong oscillator strength of the related transition. The bottom of Fig. 2 shows the experimental absorption and emission spectra measured by Ma *et al.*[25] for Si nanodots embedded in a $SiO_2$ matrix. A strong photoluminescence peak appears around 1.5 eV. Comparison of the experimental spectra with our results suggests that the presence of a Si—O—Si bridge bond at the
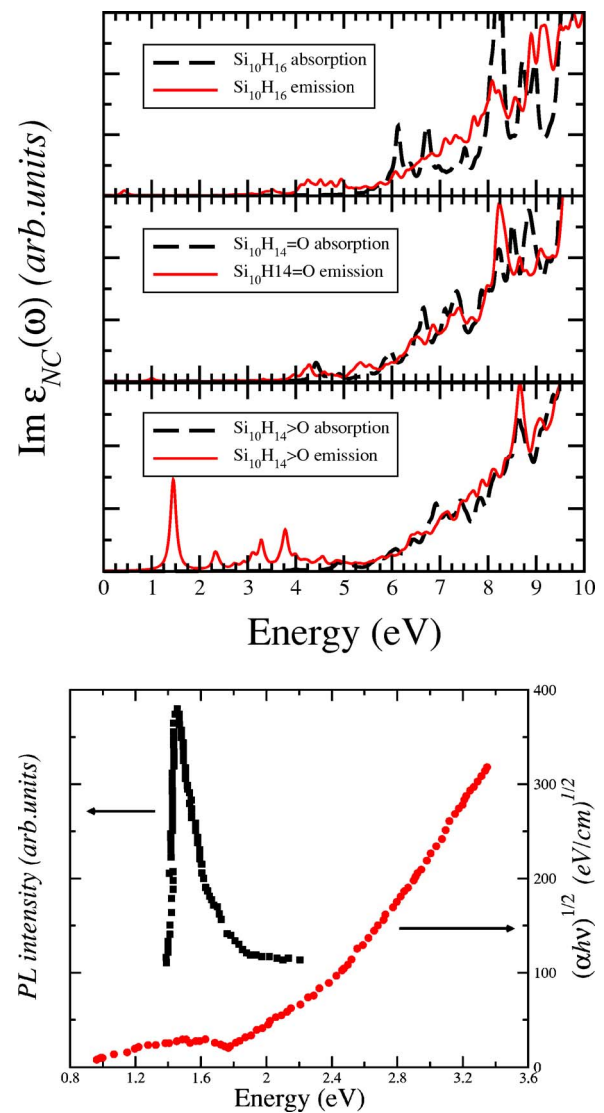


FIG. 2. (Color online) Top: emission [solid (red) line] and absorption [dashed (black) line] spectra: imaginary part of the dielectric function for the three considered Si-nc. $Si_{10}H_{16}$ (top panel), $Si_{10}H_{14}$=O (central panel), and $Si_{10}H_{14}$>O (bottom panel). Bottom: experimental results for emission (left) and absorption (right) by Ref. 25.

surface of Si-nc and the relative deformation localized around the Si—O—Si bond can explain the nature of luminescence in Si nanocrystallites: only in this case does the presence of an excitonic peak in the emission-related spectra, redshifted with respect to the absorption onset, provide an explanation for both the observed SS and the near-visible PL in Si-nc. These conclusions are supported by Fig. 3 which shows the real-space probability distribution $|\psi_{exc}(r_e, r_h)|^2$ for the bound exciton as a function of electron position $r_e$ when the hole is fixed in a given position $r_h$ (the cross in the figure). We see that the bound exciton is mainly localized around the cage distortion. Similar conclusions can be reached for the larger $Si_{29}$ nanocrystals. Figure 4 shows the calculated absorption and emission spectra for the $Si_{29}H_{34}$>O cluster, where the O atom is placed in a bridge position as in the $Si_{10}H_{14}$>O case. Also in this case starting
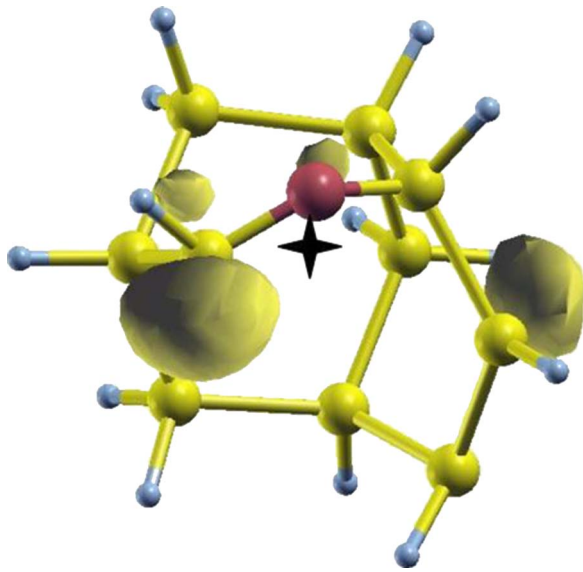
FIG. 3. (Color online) Geometrical structure of the $Si_{10}H_{14}>O$ in the excited-state configuration. Gray (yellow) balls represent Si atoms, and the dark gray (red) ball is the O atom, while the small gray (gray) balls are the hydrogens used to saturate the dangling bonds. The gray (yellow gray) isosurface gives the probability distribution $|\psi_{exc}(r_e,r_h)|^2$ for finding the electron when the hole is fixed in a given position, represented by the dark cross.

from the $Si_{29}H_{36}$ cluster only in the case of O in bridge position is there a cage distortion at the interface that allows the presence of significant emission features in the optical region. It is worthwhile to stress that the role of the interface has been experimentally proven to be important for the PL properties of embedded Si-nc in $SiO_2$ (Ref. 26) and in the mechanism of population inversion at the origin of the opti-
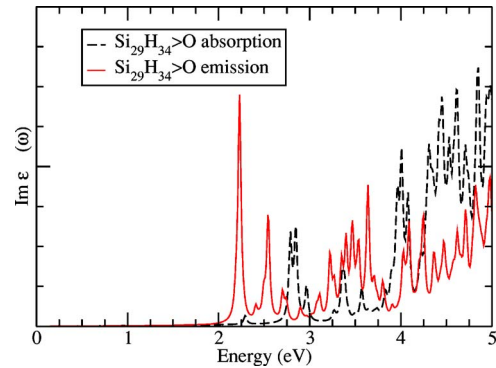


FIG. 4. (Color online) Emission (solid line) and absorption (dashed line) spectra: imaginary part of the dielectric function for the $Si_{29}H_{34}>O$ cluster.

cal gain;[26,27] besides, Monte Carlo approaches have demonstrated that Si—O—Si bridge bonds are the main building blocks in the formation of Si—$SiO_2$ flat interfaces[28] and form the low-energy geometries at the interface for Si-nc embedded in silicon dioxide.[29]

In conclusion, our theoretical results, obtained by *ab initio* calculations and fully including excitonic effects, suggest that the Si—O—Si bridge bond is responsible for the strong PL peak experimentally observed and shed some light on the role of Si-nc-$SiO_2$ interfaces.

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