Excitons in Silicon Nanocrystallites: the Nature of Luminescence

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(Dated: February 5, 2008)

Abstract

The absorption and emission spectra of silicon nanocrystals up to 1 nm diameter including geometry optimization and the many-body effects induced by the creation of an electron-hole pair have been calculated within a first-principles framework. Starting from hydrogenated silicon clusters of different size, different Si/O bonding at the cluster surface have been considered. We found that the presence of a Si-O-Si bridge bond originates significative excitonic luminescence features in the visible range that are in fair agreement with the experimental outcomes.
Following the initial impulse given by the discovery of photoluminescence (PL) from porous silicon\textsuperscript{1}, nanostructured silicon has received extensive attention\textsuperscript{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\textsubscript{2}, has given further impulse to these studies\textsuperscript{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 \textit{et al.}\textsuperscript{5} and G. Allan \textit{et al.}\textsuperscript{6} stressed the importance of bond distortion at the Si-nc surface in the excited state (ES) in creating an intrinsic localized state responsible of the PL emission. Wolkin \textit{et al.}\textsuperscript{7} observed that also oxidation introduces states in the gap, which pin the transition energies. They and others\textsuperscript{8,9} suggest that the formation of a Si=O double bond is responsible of the RS upon oxidation of the optical absorption edge. On the contrary, Vasiliev \textit{et al.}\textsuperscript{10} showed that absorption gaps of similar size can be obtained also for O connecting two Si atoms (bridge bond) at the Si-nc surface. Recently Gatti and Onida\textsuperscript{11} considered six small different prototypical oxidized Si clusters and found results similar to those of\textsuperscript{8,9}, i.e. that the RS of the absorption edge is much more pronounced in the case of the double Si=O bond that for bridge bonds. Ramos \textit{et al.}\textsuperscript{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 the experimental results and the most interesting ones are relative to PL measurements, thus are strictly related to excited state results. To date very few papers have addressed the issue of the 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 $\Delta$SCF method\textsuperscript{13,14,15,16}, where total energies are calculated both in the ground (GS) and excited states (ES). Here the ES corresponds to the electronic configuration in which the highest occupied single-particle state (HOMO) contains a hole ($h$), while the lowest unoccupied single-particle state (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, that 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 GS and ES optimized geometry, we have evaluated the optical response \( Im \left[ \varepsilon_{NC}(\omega) \right] \) (the imaginary part of the nanocrystal dielectric function) through first-principle calculations also beyond the one-particle approach. We consider the self-energy corrections by means of the GW method and the excitonic effects through the solution of the Bethe-Salpeter (BS) equation. The effect of local fields (LF) is also included, to take into account the inhomogeneity of the systems. In this work, the emission spectrum has been calculated, in a first approximation, as the time reversal of the absorption. Strictly speaking, \( Im \left[ \varepsilon_{NC}(\omega) \right] \) corresponds to an absorption spectrum in a new structural geometry, the ES geometry, with the electronic configuration of the GS. For the first time, 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, account both for the observed absorption and PL spectra. The procedure is exemplified for Si-nc of different size, a small \( \text{Si}_{10}\text{H}_{16} \) (0.55 nm diameter) and a larger \( \text{Si}_{29}\text{H}_{36} \) clusters (0.9 nm diameter). We demonstrate that light emission in the near-visible range of Si-nc is related to the presence at the Si-nc surface of Si-O-Si bridge bonds. Actually we find that a strong excitonic peak at about 1.5 eV emission energy is obtained in the \( \text{Si}_{10}\text{H}_{16} \) cluster in the presence of a Si-O-Si bridge bond as result of a considerable bond distortion on the electron-hole interaction, while the emission corresponding to the Si=O double bond 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 \( \text{Si}_{29}\text{H}_{36} \) cluster.

The starting configuration for all clusters is the hydrogenated structure (the \( \text{Si}_{10}\text{H}_{16} \) and the \( \text{Si}_{29}\text{H}_{36} \) ones); next, we consider two types of Si/O bonds at the clusters surface: the silanone-like Si=O bond (\( \text{Si}_{10}\text{H}_{14}\text{=O} \) and \( \text{Si}_{29}\text{H}_{34}\text{=O} \)) and the Si-O-Si bridge bond, where the O atom is in between two Si atoms as in the SiO\(_2\) (\( \text{Si}_{10}\text{H}_{14}\text{>O} \) and \( \text{Si}_{29}\text{H}_{34}\text{>O} \)). It is worth to note that this type of bridge bond has been demonstrated to lead to the stablest isomer configuration by Gatti and Onida. Full relaxation with respect to the atomic positions is performed for all systems both in the ground and excited configurations. Figure presents
the relaxed optimized structures of the considered Si$_{10}$ based clusters in their electronic GS and ES configuration. The ionic relaxation has produced structural changes with respect to the initial geometry which strongly depend on the type of surface termination.

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 parenthesis also the lowest dark transitions (when present) are given. All values are in eV.

|                  | Absorption         | Emission         |
|------------------|--------------------|------------------|
|                  | LDA    GW BS-LF    | 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) |

In Si$_{10}$H$_{16}$, some distortions occur at the surface in the excited state as compared to the ground state geometry, and the Si-Si distances in the core shells are somewhat concerned 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. The outcomes are similar for the larger Si$_{29}$ based clusters.

The only difference is that now the distortion induced by the promotion of an electron in the excited state is smaller, as expected, since for large clusters the charge density perturbation is distributed throughout all 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 II where the calculated optical gaps (energy differences between LUMO and HOMO) at different levels of approximation are reported for both the Si$_{10}$ and Si$_{29}$ based nanocrystals. Concerning the transition energy values of Table II we see that, going from LDA to GW, the main results common to the absorption and emission cases are the opening of the band-gap by amounts weakly dependent on the surface termination but much larger
than the corresponding 0.6 eV Si bulk case. Looking at the BS-LF calculations, we note a sort of compensation (more evident in the GS than in the ES) of self-energy and excitonic contributions: the BS-LF values return similar to the LDA ones. This compensation has been predicted theoretically by Delerue et al.\textsuperscript{22} in zero-dimensional nano-materials. The only exception are the BS-LF calculations for the excited state geometries of the clusters in the presence of the Si-O-Si bridge bonds.

Concerning the absolute values of all the absorption and emission gaps it is worthwhile to note that whereas absorption predicts the correct trend as function of size (i.e. larger gap for smaller Si-nc) this is not the case of emission, where the situation is more complex. This is due to the significant cluster distortion present 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\textsuperscript{23}. This fact has been previously discussed for the case of fully hydrogenated Si-nc, where, by total energy calculations\textsuperscript{14,15,16}, it has been demonstrated that the usual trend is recovered also for the emission for Si-nc with diameter ≥ 1 nm. Having the absorption and emission gaps, we can now give an estimate of the Stokes shift fully including excitonic effects (the BS-LF results). Going from the ground to the excited state geometry for the Si\textsubscript{10} based clusters, the fully hydrogenated clusters show a remarkable Stokes shift (4.8 eV) 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\textsubscript{29} based clusters, 2.5 eV and 0.1 eV respectively. It should be noted that if the SS 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\textsubscript{10}H\textsubscript{14}=O cluster we would obtain a weaker SS (1.7 eV) and for the Si\textsubscript{29}H\textsubscript{34} >O cluster a stronger SS (2.0 eV)\textsuperscript{23}. A clearer insight on these results is offered by Fig. 2, where the calculated absorption and emission spectra for all the Si\textsubscript{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 remain similar for the fully hydrogenated Si\textsubscript{10}H\textsubscript{16} (top panel) cluster and for the Si\textsubscript{10}H\textsubscript{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 the 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 a clear PL peak appears 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. for Si-nanodots embedded in SiO$_2$ matrix. A strong photoluminescence peak appears around 1.5 eV.

Comparison of the experimental spectra with our results suggest that the presence of a Si-O-Si bridge bond at the 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 the presence of an excitonic peak in the emission related spectra, red shifted with respect to the absorption onset, provides an explanation for both the observed Stokes Shift 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 the electron position $r_e$ when the hole is fixed in a given position $r_h$ (the dark 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. Fig. 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 from the Si$_{29}$H$_{36}$ cluster only in the case of O in bridge position there is 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$_2$ and in the mechanism of population inversion at the origin of the optical gain, 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 and form the low energy geometries at the interface for Si-nc embedded in silicon dioxide.

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$_2$ interface.
This work is supported by MIUR (NANOSIM and PRIN 2005), by CNISM, and by the EU through the NANOQUANTA Network of Excellence (Contract No. NMP4-CT-2004-500198). We acknowledge CINECA CPU time granted by INFM (Progetto Calcolo Parallelo). Bethe-Salpeter calculations have been performed using the EXC code http://www.bethe-salpeter.org/.

1. L. T. Canham, Appl. Phys. Lett. 57, 1046 (1990).
2. O. Bisi, S. Ossicini, and L. Pavesi, Surf. Sci. Reports 38, 5 (2000).
3. S. Ossicini, L. Pavesi, F. Priolo, ”Light Emitting Silicon for Microphotonics”, Springer Tracts on Modern Physics 194, Springer-Verlag Berlin (2003).
4. L. Pavesi, L. Dal Negro, C. Mazzeneli, G. Franzó, F. Priolo, Nature 408, 440 (2000); L. Dal Negro, M. Cazzanelli, L. Pavesi, S. Ossicini, D. Pacifici, G. Franzò, F. Priolo, and F. Iacona, Appl. Phys. Lett. 82, 4636 (2003).
5. R. J. Baierle, M. J. Caldas, E. Molinari, and S. Ossicini, Solid State Commun. 102, 545 (1997).
6. G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. 76, 2961 (1996).
7. M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C Delerue, Phys. Rev. Lett. 82, 197 (1999).
8. A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli, Phys. Rev. Lett. 88, 097401 (2002).
9. M. Luppi, and S. Ossicini, J. Appl. Phys., 94, 2130 (2003), Phys. Rev. B 71, 035340 (2005).
10. I. Vasiliev, J. R. Chelikowsky, and R.M. Martin, Phys. Rev. B 65, 121302(R) (2002).
11. M. Gatti, G. Onida, Phys. Rev. B 72, 045442 (2005).
12. L. Ramos, J. Furthmüller, F. Bechstedt, Appl. Phys. Lett. 87, 143113 (2005).
13. E. Luppi, E. Degoli, G. Cantele, S. Ossicini, R. Magri, D. Ninno, O. Bisi, O. Pulci, G. Onida, M. Gatti, A. Incze, R. Del Sole, Opt. Mater. 27, 1008 (2005).
14. A. Puzder, A. J. Williamson, J. C. Grossman, G. Galli, J. Am. Chem. Soc. 125, 2786 (2003).
15. A. Franceschetti, S. T. Pantelides, Phys. Rev. B 68, 033313 (2003).
16. E. Degoli, G. Cantele, E. Luppi, R. Magri, D. Ninno, O. Bisi, S. Ossicini, Phys. Rev. B 69, 155411 (2004).
17. L. Hedin, Phys. Rev. 139, A796 (1965).
18. G. Onida, L. Reining, and A. Rubio, Rev. of Mod. Phys. 74, 601 (2002) and references therein.
19 F. Bassani and G. Pastori Parravicini, "Electronic States and Optical Transitions in Solids", Pergamon Press, New York 1975.

20 The Si$_{10}$H$_{14}$ >O cluster we considered here corresponds to the Si$_{10}$H$_{14}$O-sym o$_{11}$, where O make a bridge between "second neighbors" Si atoms. We have obtained similar results have for the Si$_{10}$H$_{14}$O-asym case, where O is in between two "first neighbors" Si atoms.

21 The DFT calculations have been performed using the ESPRESSO package: S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari, A. Kokalj, http://www.pwscf.org/.

22 C. Delerue, M. Lannoo, and G. Allan, Phys. Rev. Lett. 84, 2457 (2000).

23 A careful discussion about the role of size on the many-body effects and of structural deformation on the optical spectra will be presented in O. Pulci et al., to be published.

24 Z. Ma, X. Liao, G. Kong, J. Chu, Appl. Phys. Lett. 75, 1857 (1999).

25 N. Daldosso, M. Luppi, S. Ossicini, E. Degoli, R. Magri, G. Dalba, P. Fornasini, R. Grisenti, F. Rocca, L. Pavesi, S. Boninelli, F. Priolo, C. Spinella, and F. Iacona, Phys. Rev. B 68, 085327 (2003).

26 L. Dal Negro, M. Cazzanelli, L. Pavesi, S. Ossicini, D. Pacifici, G. Franzù, F. Priolo, and F. Iacona, Appl. Phys. Lett. 82, 4636 (2003).

27 Y. Tu, and J. Tersoff, Phys. Rev. Lett. 89, 086102 (2002).

28 G. Hadjisavvas, and P. Kelires, Phys. Rev. Lett. 93, 226104 (2004).
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-state (right panels). Grey (yellow) balls represent Si atoms, the black (red) ball is the O atom, while the small grey (grey) balls are the hydrogens used to saturate the dangling bonds.
FIG. 2: Up: Emission (solid (red) line) and absorption (dashed (black) line) spectra: imaginary part of the dielectric function for the three considered Si-nc. $\text{Si}_{10}\text{H}_{16}$ (top panel), $\text{Si}_{10}\text{H}_{14}=\text{O}$ (central panel) and $\text{Si}_{10}\text{H}_{14}>\text{O}$ (bottom panel). Down: experimental results for emission (left) and absorption (right) by [24].
FIG. 3: Geometrical structure of the Si$_{10}$H$_{14}$ >O in the excited state configuration. Grey (yellow) balls represent Si atoms, the dark grey (red) ball is the O atom, while the small grey (grey) balls are the hydrogens used to saturate the dangling bonds. The grey (yellow grey) isosurface give 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.
FIG. 4: Emission (solid line) and absorption (dashed line) spectra: imaginary part of the dielectric function for the Si$_{29}$H$_{34}$ > O cluster.