Doping in silicon nanocrystals: An ab initio study of the structural, electronic and optical properties

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Available online 26 September 2006

Abstract

There are experimental evidences that doping control at the nanoscale can significantly modify the optical properties with respect to the pure systems. This is the case of silicon nanocrystals (Si-nc), for which it has been shown that the photoluminescence (PL) peak can be tuned also below the bulk Si band gap by properly controlling the impurities, for example by boron (B) and phosphorus (P) codoping. In this work, we report on an ab initio study of impurity states in Si-nc. We consider B and P substitutional impurities for Si-nc with a diameter up to 2.2 nm. Formation energies (FEs), electronic, optical and structural properties have been determined as a function of the cluster dimension. For both B-doped and P-doped Si-nc the FE increases on decreasing the dimension, showing that the substitutional doping gets progressively more difficult for the smaller nanocrystals. Moreover, subsurface impurity positions result to be the most stable ones. The codoping reduces the FE strongly favoring this process with respect to the simple n-doping or p-doping. Such an effect can be attributed to charge compensation between the donor and the acceptor atoms. Moreover, smaller structural deformations, with respect to n-doped and p-doped cases, localized only around the impurity sites are observed. The band gap and the optical threshold are largely reduced with respect to the undoped Si-nc showing the possibility of an impurity-based engineering of the Si-nc PL properties.

PACS: 73.22–f; 71.15.m

Keywords: Nanocrystals; Doping; Luminescence

1. Introduction

During the last 10 years, various experimental and theoretical results have raised hopes for a real employment of nanostructured silicon as an optical active material \cite{1}. The idea stems from the possibility of confining carriers into tiny silicon nanocrystals (Si-nc) (1–4 nm in size) and to use quantum confinement effects to change the physical properties of bulk silicon. In particular, it has been observed that Si-nc band gap increases with decreasing size and visible luminescence external efficiency in excess of 10% has been obtained \cite{1,2}. Moreover, optical gain in Si-nc has been demonstrated in a variety of situations \cite{3}. Nevertheless, Si-nc still remain indirect band gap materials where structures related to momentum-conserving phonons were clearly observed. This drawback can be circumvented by introducing in the Si-nc isoelectronic impurities \cite{1,2} or by codoping with n- and p-type impurities \cite{4}. In a series of intriguing papers, Fuji and collaborators \cite{4–6} have shown the possibility of controlling the photoluminescence (PL) properties of Si-nc by n- and p-type codoping, proving not only that the PL intensity of codoped (boron (B) and phosphorus (P)) Si-nc is always higher than that of either P-doped or B-doped Si-nc, but also that it is even higher with respect to the pure Si-nc. Besides, under resonant excitation conditions, the codoped samples did not exhibit structures
related to momentum-conserving phonons suggesting that in this case the quasidirect optical transitions are predominant. Theoretical studies of impurities in silicon quantum dots have lagged relative to calculations for pure, undoped systems. Only few first-principle studies are present in the literature, devoted to quantum confinement effects in Si-nc doped with the introduction of only one impurity atom [7–9]. The results point out that the ionization energy for the Si-nc is virtually size-independent while donor and acceptor binding energies are substantially enhanced.

Recently, we have performed a preliminary theoretical study considering the codoping of Si-nc with n- and p-type impurities [10]. In the present paper, we will present our recent results concerning the structural, electronic and optical properties of n-doped, p-doped and codoped Si-nc. The paper is organized as follows: in Section 2, we briefly elucidate the theoretical framework used, Section 3 is devoted to the discussion of the results and Section 4 presents our conclusions.

2. Computational methods

Our results have been obtained by using a plane-wave, pseudopotential density functional calculation of impurity states in spherical Si-nc, with diameter ranging from 1.04 nm (Si$_{29}$H$_{36}$) to 2.24 nm (Si$_{293}$H$_{172}$). The Si-nc have been built taking all the bulk Si atoms contained within a sphere of a given radius and terminating the surface dangling bonds with hydrogen. Each cluster has been centered on an Si atom. As in the experiments, we consider B and P impurities in substitutional sites. Full relaxation with respect to the atomic positions has been performed for both doped and undoped systems. All the calculations have been done using the Quantum-Espresso package [11], within the GGA approximation using Vanderbilt ultrasoft [12] pseudopotentials. The Si-nc have been embedded in a large supercell in order to prevent interactions between the periodic replicas (about 6 Å of vacuum separates neighbor clusters in all the considered systems). A careful analysis has been performed on the convergence of both the electronic and structural properties with respect to both the supercell side and plane-wave basis set cut-off.

Both the structural and electronic properties have been investigated as a function of the size and of the impurity position within the Si-nc. The impurity formation energy (FE) has been calculated as a function of the Si-nc dimension and of the impurity position within the nanocluster. Absorption properties of the Si-nc have been calculated through the imaginary part of the dielectric function.

3. Results: structural, electronic and optical properties

The structural changes of the doped Si-nc have been investigated as a function of the size of the impurity position and of the number of dopant species present within the Si-nc. The first important point is that the amount of the relaxation around the impurity is directly related to the impurity valence. A more significant distortion is obtained doping with trivalent atoms (e.g. B), in which an electron that could be used to form a bond with the surrounding Si atoms is missing. Actually, in the B-doped clusters, while the Si–Si bond lengths keep almost unchanged, some reconstruction occurs around the impurity. The overall structure has $C_{3v}$ symmetry, with an impurity displacement along the $\langle 111 \rangle$ direction when it is placed at the nanocluster center. Such a displacement leads to one longer and three shorter (and equal) Si-impurity distances. While the longer bond is “almost” independent of the Si-nc size, the shorter one decreases with the size. It is interesting to note that the relaxation of the bulk Si supercell containing the B impurity leads to an “almost” $T_d$ configuration, in which the four B–Si bonds are practically the same. On the contrary, for pentavalent atoms, such as the P-doped Si-nc, the relaxation leads to a nearly $T_d$ symmetry, in which the differences between the four P–Si bonds are negligible, less than 0.7% [13].

Starting from the Si$_n$H$_m$ nanocluster [14], the FE for the neutral X impurity can be defined as the energy needed to insert the X atom with chemical potential $\mu_X$ within the cluster after removing a Si atom (transferred to the chemical reservoir, assumed to be bulk Si)

$$E_f = E(\text{Si}_{n-1}X\text{H}_m) - E(\text{Si}_n\text{H}_m) + \mu_{\text{Si}} - \mu_X,$$

where $E$ is the total energy of the system, $\mu_{\text{Si}}$ the total energy per atom in bulk Si, $\mu_X$ the total energy per atom of the impurity [15]. Our calculations clearly show that for smaller Si-nc, a larger energy is needed for the formation of the impurity. For B-doped Si-nc, a decreasing behavior of $E_f$ vs. $R$ is observed, that can be described by the linear formula

$$E_f = 0.796 + 4.63971/R,$$

where $R$ is expressed in Å and $E_f$ in eV, and the value $E_f = 0.796$ eV corresponds to doped Si bulk. For P-doped Si-nc, the same decreasing behavior is observed and the linear formula is now:

$$E_f = 0.21008 + 4.98131/R.$$
two longer Si-impurity distances with respect to the surface and inner Si atoms (see Table 1).

Table 1 gives the optimized bond lengths around the impurity in subsurface positions for the Si$_{87}$H$_{36}$-nc (the results are quite similar for Si$_{145}$H$_{100}$). Both n-doped or p-doped and codoped cases have been considered. It is interesting to note that in the codoped case, the differences among the four impurity-Si bond lengths are clearly smaller with respect to the n-doped or p-doped case. Thus, when carriers in the Si-nc are perfectly compensated by codoping with n- and p-type impurities, an almost $T_d$ configuration is recovered in which the four impurity-Si bonds are practically the same.

This fact is reflected in the FE results reported in Fig. 1, for B-doped, P-doped and B-P-codoped Si-nc for two, different in size, nanocrystals. In all cases the impurities are located in subsurface positions. In the figure, dashed lines connect the FE values obtained when neutral impurities are located at the largest possible distance in the codoped nanoclusters, while solid lines are used for the cases in which the impurities are located at subsurface positions. In the figure, dashed lines are related to the Si$_{87}$H$_{36}$ nanoclusters, circles (red and blue) to the Si$_{145}$H$_{100}$ ones. Extensions, whereas the $E_G$ have been evaluated also for various B- and P-codoped Si-nc; e.g. we have observed a reduction of $E_G$ from 2.59 (for the pure Si-nc Si$_{87}$H$_{36}$) to 1.82 eV for the codoped Si$_{86}$BPH$_{76}$ and similarly a reduction from 2.30 (for the pure Si-nc Si$_{145}$H$_{100}$) to 1.56 for the codoped Si$_{145}$BPH$_{100}$.

Obviously, for pure Si-nc larger than those considered here, having a smaller $E_G$, it would be possible by codoping to obtain an $E_G$ even smaller than the bulk Si band gap in agreement with the experimental outcomes [4,6]. Besides, on going from the pure, to the B-doped or P-doped case, to the codoped Si-nc, the HOMO and lowest occupied molecular orbital (LUMO) states progressively localize on the impurities. In the codoped case, the HOMO is strongly localized on the B impurity and the LUMO on the P impurity.

These facts have a profound influence on the optical properties of the Si-nc. The optical properties have been calculated through the imaginary part $\varepsilon_2$ of the dielectric function:

$$
\varepsilon_2(\omega) = \frac{4\pi^2e^2}{m^*c^2} \sum_{\nu,k} \frac{2}{V} |\langle \psi_{\nu,k}|p_{\nu,k}|\psi_{\nu,k}\rangle|^2 \times \delta[E_{\nu}(k) - E_{\nu}(k) - \hbar\omega],
$$

where $\omega = (\xi, \gamma, \zeta)$, $E_\nu$ and $E_c$ denote the energies of the valence $\psi_{\nu,k}$ and conduction $\psi_{c,k}$ band states at a k point ($F$ in our case), and $V$ is the supercell volume. The optical absorption coefficient

$$
\alpha(\omega) = \frac{\alpha}{nc} \varepsilon_2(\omega)
$$

is directly related to $\varepsilon_2$: thus the imaginary part of the dielectric function contains all the necessary information...
about the absorption properties of the nanocrystals. Owing to the strong confinement effects present in nanoclusters, only transitions at the $I$ point have been considered. Fig. 2 reports the calculated imaginary parts of the dielectric function ($\varepsilon_2$) for the Si$_{58}$BH$_{76}$ clusters, considering B-doped (top panel) and P-doped (center panel) nanocrystals and the B-P codoped (bottom panel) nanocrystal. For all cases, the result is compared with the corresponding one for the undoped Si$_{58}$H$_{76}$ cluster.

Concerning both the B-doped and P-doped cases, we see that several new peaks appear in the low-energy region between 0 and 2 eV. These peaks are due to the interband and intraband transitions that involve the impurity state located in the band energy gap. These new features could be important for applications in the infrared region and in Raman lasers technology. For the codoped Si$_{58}$BH$_{76}$ cluster, as shown at the bottom of Fig. 2, we note the shift of the optical gap to lower energies and the rise of new features not present for the undoped Si$_{58}$H$_{76}$ cluster. The enhancement of the intensity in this region is a direct consequence of the localization process of the HOMO and LUMO states on the impurities described above. These outcomes can explain the experimental data [4,6] that show a PL intensity for codoped Si-nc even higher than that of pure Si-nc and prove that by codoping it is possible to shift the PL peak even below the Si bulk band gap.

4. Conclusions

A detailed first-principle study of B- and/or P-doping in Si-nc has been performed analyzing their structural, electronic and optical properties as a function of size and impurity position within the cluster. We have shown that in n-doped and p-doped Si-nc, the structural deformation around the impurity depends on both the impurity valence and impurity position. The impurity subsurface positions are always the most stable ones. As a consequence of charge compensation, it is easier codoping the nanocrystal than doping it with only one type of impurity atom. The study of the electronic properties shows that for B-doped and P-doped Si-nc, the HOMO is located around the impurity, whereas the LUMO is delocalized in the nanocrystals and that the energy gap strongly depends on the impurity valence. For the B- and P-codoped Si-nc, both HOMO and LUMO are localized around the impurity sites thus strongly lowering the energy gap with respect to that of the pure silicon nanostructures. The optical properties reflect the electronic ones, thus for B-doped and P-doped nanocrystals absorption features are present in the infrared region, whereas for the case of B–P-codoping electronic transitions between donor and acceptor states in the optical region are allowed, making it possible to engineer the PL spectrum of the nanocrystals that will depend on the nanocrystal size.

Acknowledgements

We acknowledge the support of the MIUR PRIN (2005) Italy and of the CRUI Vigno Project (2005) Italy–Germany. All the calculations were performed at CINECA-Bologna (“Iniziativa Calcolo Parallelo del CNR- INFM”), CICAIA-Modena and “Campus Computational Grid”-Università di Napoli “Federico II”.

References

[13] Calculations have been done also for isovalent impurity (C and Ge) and other group III (Al) and group V (N) impurities; in general, trivalent impurity tends to lower the symmetry down to a $C_3v$ one while an almost Td symmetry is preserved for isovalent and pentavalent impurities. A role seems to be played also by the impurity dimension: in B-doped, C-doped and N-doped clusters, the Si-impurity bond lengths are shorter with respect to typical Si-Si bond-length in the undoped cluster while the Si-P, Si-Al and Si-Ge distances are slightly larger. An extensive study can be found in L.E. Ramos, E. Degoli, G. Cantele, S. Ossicini, D. Ninno, J. Furthmüller, F. Bechstedt Phys. Rev. B, submitted.


[15] We consider the total energy per atom in the tetragonal $B_{50}$ crystal for B, and the orthorhombic black phosphorus for P.