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First-principles study of *n*- and *p*-doped silicon nanoclusters

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We report on an *ab initio* study of the structural and electronic properties of B- and P-doped Si nanoclusters. The neutral impurities formation energies are calculated. We show that they are higher in smaller nanoclusters and that this is not related to the structural relaxation around the impurity. Their dependence on the impurity position within the nanocluster is also discussed. Finally, we have calculated the B and P activation energies showing the existence of a nearly linear scaling with the nanocluster inverse radius. Interestingly, no significant variation of the activation energy on the impurity species is found and the cluster relaxation gives a minor contribution to it.

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The possibility of enhancing the electrical conductivity of nanosized systems has been largely studied. For example, it is known that porous Si is obtained from bulk *n*- or *p*-doped Si by means of an electrochemical etching. Nevertheless, even for the larger (mesoporous) samples, a very low conductivity is measured, despite the fact that the etching process does not remove the impurities from the system.[1] This suggests that the ionization of the impurities at room temperature is strongly quenched with respect to the bulk. Therefore, the possibility of generating free charge carriers from defect states is limited by size effects, even if it has been experimentally shown that the reactivation of the charge carriers is possible.[2–4] A full understanding of the trapping and detrapping mechanisms has not yet been reached and further work is required.

To address these important questions we explore here the quantum confinement effects on the activation energy of acceptor and donor states in silicon nanoclusters (Si-nc) and investigate also how the reduced dimensionality affects the impurity solubility through calculations of the dopant formation energy.

From the theoretical point of view, very few atomistic studies concerning impurity states in nanosized systems are present in the literature, many of them based on semiempirical approaches. In Ref. 5 an empirical LCAO calculation of the activation energies of hydrogenic impurities in nanocrystalline Si is discussed, while quantum confinement in P-doped Si-nc is analyzed in Ref. 6, using a real-space, *ab initio* pseudopotential density functional method.

In this paper we discuss a plane-wave, pseudopotential density functional calculation of impurity states in spherical Si-nc, with radius ranging from 0.52 nm ($Si_{29}H_{36}$) to 1.12 nm ($Si_{293}H_{172}$). We consider B and P impurities in substitutional sites. Both the structural and electronic properties are investigated as a function of the size and of the impurity position within the Si-nc. The impurity formation energy is calculated as a function of the Si-nc dimension, showing that, due to size effects, the insertion of an impurity within a nanocluster requires more energy than in the bulk system. Indeed, we show that the formation energy is a decreasing function of the size. The impurity activation energy is calculated, and it results that it has a nearly linear scaling with the Si-nc inverse radius. Thus, the creation of free carriers is made more difficult by the reduced dimensions of the Si-nc, as observed experimentally.

The Si-nc are 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 is centered on a Si atom. Full relaxation with respect to the atomic positions is performed for both doped and undoped systems. All the calculations have been performed using the ESPRESSO package[7] within the GGA approximation using Vanderbilt ultrasoft[8] pseudopotentials. The Si-nc have been embedded in large supercells 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 cutoff. The total energy for the charged systems has been calculated including the Makov-Payne correction,[9] checking that the final energy is independent of the supercell side. This allows us to consider energy differences, overcoming the well-known problems associated with not real-space approaches.[6] Finally, the Si-nc volume is determined as the number of Si atoms times the volume per atom in bulk Si.

Starting from the Si_nH_m nanocluster,[10] the formation energy for the neutral X impurity can be defined as the energy needed to insert the X atom with chemical potential μ_X within the cluster after removing a Si atom (transferred to the chemical reservoir, assumed to be bulk Si)[11]

$$E_f = E(Si_{n-1}XH_m) - E(Si_nH_m) + \mu_{Si} - \mu_X, \qquad (1)$$

where E is the total energy of the system, μ_{Si} is the total energy per atom of bulk Si, and μ_X is the total energy per atom of the impurity (we consider the total energy per atom

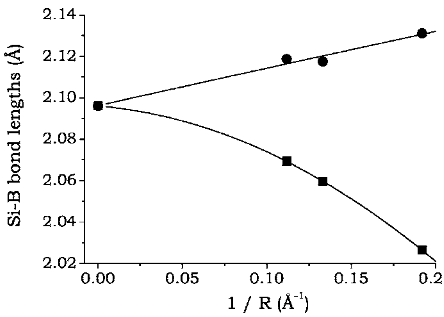

FIG. 1. The B-Si bond length as a function of the cluster inverse radius. The lines are guides for the eyes. The two sets of data correspond to the longer (circles) and the three shorter (squares) bonds. The impurity is at the cluster center.

in the tetragonal B_{50} crystal for B, as in Ref. 12, and the orthorhombic black phosphorus for P, as in Ref. 13).

First of all, it is interesting to look at the change of the structural properties induced by the impurity presence. For 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 displacement leads to one longer and three shorter (and equal) Si-impurity distances, as shown in Fig. 1. The zero radius corresponds to bulk Si (for which a 64-atom supercell, and a $4\times4\times4$ grid for k-space sampling has been considered[12]). While the longer bond is "almost" independent of the size, the shorter one is increasing 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.[14] The relaxation of the P-doped Si-nc leads to a nearly T_d symmetry,[6] in which the differences between the four P-Si bonds are negligible (the Si-P bond shows a maximum variation of about 0.7%, ranging from 2.365 Å in the bulk Si supercell to about 2.38 Å in the smallest cluster, while the calculated Si-Si bond length in bulk Si is 2.367 Å). Also, we have tried to relax an Al and an As impurity located at the $Si_{29}H_{36}$ cluster center, and found one longer and three shorter bonds (about a 6% difference) in the case of Al, and four very similar bonds in the case of the As atom. Therefore, it seems that the amount of the relaxation around the impurity is directly related to the impurity valence. It is interesting that a more significant distortion is found for the trivalent atoms (B and Al), for which one electron for the bonding with the surrounding Si atoms is missing.

The formation energy for the neutral impurity at the cluster center, as calculated from Eq. (1), is reported in Fig. 2, for both (a) B- and (b) P-doped Si-nc, as a function of the inverse radius of the system. In order to bring out the effect of the Si-nc relaxation, three different sets of data are presented. In the first situation (filled squares) both the total energies in Eq. (1) are calculated keeping the Si-Si and Si-X distances within the cluster fixed at the Si-Si bond length in bulk Si, while the passivating H atoms at the surface are along the bulk Si-Si bond directions at the Si-H distance as calculated from the SiH_4 molecule. In the second case (empty circles) we first relaxed the undoped Si-nc, then its optimized geometry has been used for the doped nanocluster, thus neglecting the effects of the relaxation around the impurity. In the third situation (empty triangles) the doped nanocluster has been fully relaxed after the insertion of the impurity.

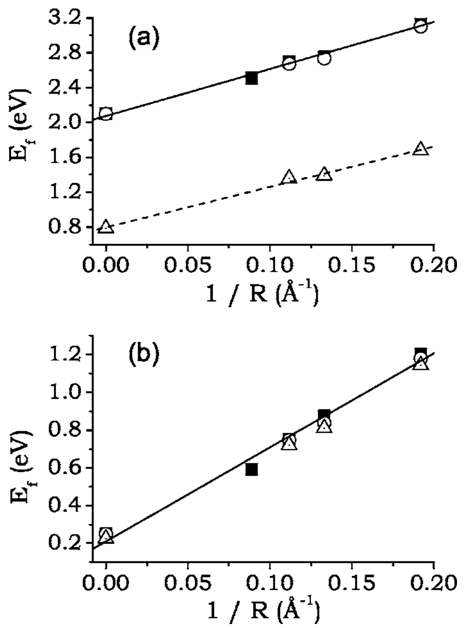

FIG. 2. Formation energy of the neutral impurities at the cluster center, as calculated from Eq. (1), as a function of the inverse nanocluster radius. Both (a) B- and (b) P-doped nanoclusters are considered. The three sets of data correspond to total energies in Eq. (1) calculated for three different geometries: (i) both doped and undoped nanoclusters have not been relaxed, filled squares; (ii) only the undoped cluster has been relaxed, empty circles; (iii) both clusters have been relaxed, empty triangles. The zero inverse radius corresponds to bulk Si. The lines are linear fits of the corresponding set of data (see the text).

From Fig. 2(a) it is seen that for B-doped Si-nc, E_f is a decreasing function of the size, demonstrating that for larger systems the substitutional impurity is more stable. For the relaxed bulk system we get a formation energy of 0.8 eV, in fair agreement with 0.9 eV calculated in Ref. 12. The solid line is a linear fit to the first set of the data ($E_f=2.073\,25+5.403\,48/R$, where R is expressed in Å and E_f in eV) while the dashed line is a linear fit for the third set of data ($E_f=0.796+4.639\,71/R$). The second set of data shows negligible variations with respect to the first one.

For P-doped Si-nc the same decreasing behavior of E_f vs $1/R$ is observed, as shown in Fig. 2(b). The solid line is, again, a linear fit of the first set of data ($E_f=0.210\,08+4.981\,31/R$).

Two main points should be highlighted here. The first one is that, at fixed R, the atomic relaxation around the B impurity induces a significant reduction of the formation energy, which is nearly independent of the nanocluster size. The same reduction is, of course, observed for P-doped nanoclusters, even if it is much less evident. The second point is that the variation of the formation energy with $1/R$ cannot be attributed to the atomic relaxation around the impurity. Actually it is just a size effect, because even without any relax-

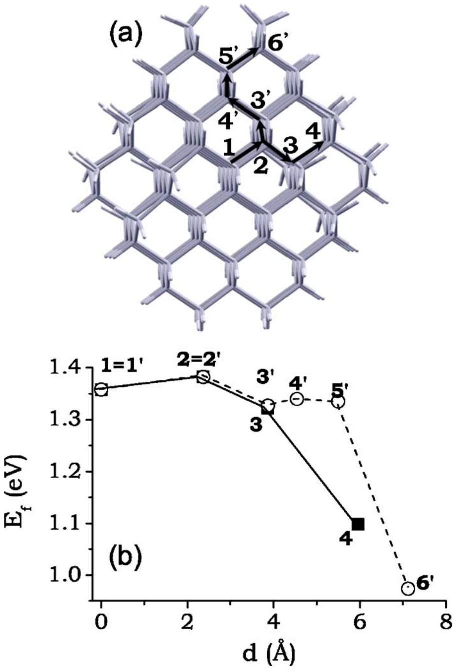

FIG. 3. (Color online) Formation energies for neutral impurities as a function of the impurity position within the cluster (b). The impurity is moved along two different paths toward the surface, as shown in (a). The lines are guides for the eyes.

ation (see the filled squares in Fig. 2) it is still present.

It is worth pointing out that the size dependence of the calculated formation energy is in qualitative agreement with the observed suppression of the photoluminescence (PL) in doped Si nanocrystals (Si-nc). Fujii *et al.*[15] have shown that on increasing the annealing temperature both the Si-nc size increases and a stronger PL suppression is observed. This effect is a signature of a higher impurity concentration, thus showing that larger Si-nc can more easily sustain the doping.

It can be interesting to see how the formation energy changes as a function of the impurity position within the Si-nc. In Fig. 3 we show the formation energy for the B neutral impurity in the $Si_{146}BH_{100}$ cluster. The impurity is moved from the cluster center toward the surface along two paths, shown in Fig. 3(a). The calculated energies are shown in Fig. 3(b). On the x axis we put the distance from the center of the replaced Si atom in the $Si_{147}H_{100}$ cluster. It comes out that as far as the internal core is concerned, variations not higher than 0.06 eV are found. On the contrary, an energy drop of either 0.25 eV ($3 \rightarrow 4$) or 0.35 eV ($5' \rightarrow 6'$) is found as the B impurity is moved to the Si layer just below the surface. This is explained by considering that such positions are the only ones that allow a significant atomic relaxation around the impurity, because in the other cases the surrounding Si cage is quite stable. Thus, as the B atom is moved toward the surface the formation energy decreases, making the subsurface positions more stable.

The impurity activation energy is calculated using the formula[6]

$$E_{\mathrm{act}}(B) = I_u - A_d,$$

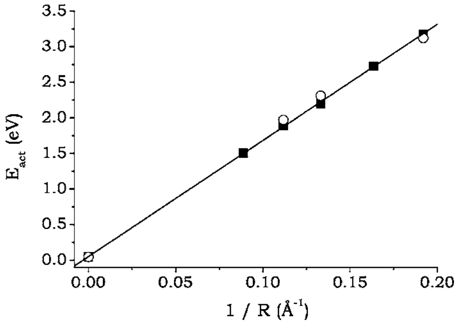

FIG. 4. Impurity activation energy, as a function of the inverse nanocluster radius. Both B- (filled squares) and P-doped (open circles) Si-nc are considered. The zero inverse radius corresponds to bulk Si. The solid line is a linear fit of the data for the B-doped clusters. The impurity is at the cluster center.

$$E_{\mathrm{act}}(P) = I_d - A_u, \tag{2}$$

where $I = E(n-1) - E(n)$ and $A = E(n) - E(n+1)$ give the nanocluster ionization energy and electron affinity, respectively, while the subscripts u and d refer to the pure (undoped) and doped system, respectively. The size dependence of I_u and A_u agrees with the fits reported in Ref. 16. Our calculated activation energy is shown in Fig. 4 for both B- and P-doped Si-nc (impurity at the cluster center[17]). The solid line is a linear fit of the data relative to B. The main point here is that a linear scaling of this energy with the inverse cluster radius is found, giving an indication that the main contribution to this energy is due to the almost unscreened Coulomb interaction,[18] leading to a very localized nature of the impurity states, as found in Ref. 6. Moreover, the cluster relaxation does not significantly affect this energy. The linear fit in Fig. 4 provides the activation energy for any nanocrystal dimension. We obtain

$$E_{\mathrm{act}} = 0.050\,904 + \frac{16.298\,819}{R}, \tag{3}$$

where R is in Å and E_{act} is in eV. The interpolation formula (3) has been calculated by including the experimental value of the activation energy in bulk Si (0.045 eV for both B and P impurities[19]). Nevertheless, if the point $1/R = 0$ is skipped in the fit, the interpolation formula provides for the bulk 0.07 eV. This can be considered a good estimation because the activation energy for the bulk cannot be given with an error of less than 0.1 eV.[12] It is also worth mentioning that the activation energy for P-doped clusters is in fair agreement with those calculated in Ref. 6. This figure shows why impurity ionization is strongly quenched for Si-nc with respect to the bulk.[1] From Eq. (3) we find that the impurity activation energy in a Si-nc of 1.8 (2.3) nm radius is about 1 (0.75) eV, much larger than the bulk one.

In conclusion, we have reported on a detailed first-principle calculation of the impurity states in B- and P-doped Si-nc. The formation energies for neutral impurities have been discussed as a function of both the size and position within the Si-nc. It has been shown that for smaller Si-nc a larger energy is needed for the formation of the impurity.

Moreover, moving the impurity from the cluster center, the formation energy gets lower, thus substitutional positions near the surface are more stable. We have found that the activation energy is a decreasing function of the size, showing that for the smaller Si-nc it would be very difficult to electrically activate the impurities. Finally, we have shown that all these findings are closely related to size effects and not to the relaxation of the Si atoms around the impurity, because the main size-dependent features keep unchanged if unrelaxed nanoclusters are considered.

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