

P and B single- and co-doped Silicon Nanocrystals: Formation and Activation Energies, Electronic and Optical Properties

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We report on an *ab initio* study of the structural and electronic properties of B and P doped Si nanocrystals (Si-nc). The formation energies (FE) scale with the radius, the activation energies with the inverse radius. The effects of B and P co-doping show that the FE are always smaller than that for the corresponding single-doped cases and that is possible to engineer the photoluminescence properties of Si-nc.

Since semiconductor optoelectronic devices are moving towards nanometric dimensions, it becomes more and more important to understand the properties of semiconductors at the nanoscale, where quantum confinement effects become predominant. These effects render Si-nc capable of high photoluminescence quantum yield in comparison with the corresponding bulk, beside optical gain has been observed for Si-nc opening the door to Si based lasers. The main limitation to high photoluminescence efficiency is related to radiationless Auger recombination in the Si-nc, that can be circumvented by introducing in the Si-nc an isoelectronic impurity or by simultaneous *n*- and *p*-type impurity doping [1]. Moreover the performance of a semiconductor is controlled by shallow dopants; through the introduction of shallow impurities it is thus possible to engineer their electrical and optical properties. In this paper we discuss a plane-wave, pseudopotential density functional calculation of impurity states in silicon spherical nanoclusters (Si-nc), with radius ranging from 0.52 nm (Si₂₉H₃₆) to 1.12 nm (Si₂₉₃H₁₇₂). 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 nanocluster. Starting from the Si_nH_m-nc, the formation energy (FE) of the neutral B or/and P impurities can be defined as the energy needed to insert one B and/or one P atom within the cluster after removing one (or two) Si atoms (transferred to the chemical reservoir, assumed to be bulk Si) [2]

$$\Delta E_f = E(\text{Si}_{n-l-k}\text{B}_k\text{P}_l\text{H}_m) - E(\text{Si}_n\text{H}_m) + (k+l)\mu_{\text{Si}} - k\mu_{\text{B}} - l\mu_{\text{P}} \quad (1)$$

where E is the total energy of the system, μ_{Si} the total energy per atom of bulk Si, $\mu_{\text{B(P)}}$ the total energy per atom of the impurity. The formation energy for the neutral impurity, as calculated from eq. (1), is reported in Fig. 1

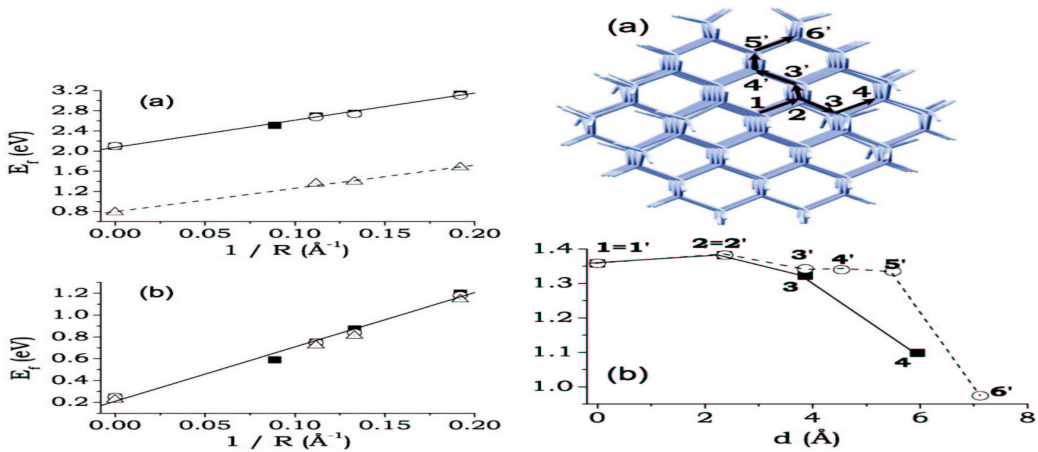


FIG. 1: **Left:** Formation energy of the neutral impurities, as calculated from eq. (1), as a function of the inverse nanocluster radius. Both (a) B- and (b) P-doped nanoclusters are considered. The three sets of data correspond to different geometries: i) both the doped and undoped nanocluster have not been relaxed, filled squares; ii) only the undoped cluster has been relaxed, empty squares; iii) both clusters have been relaxed, empty triangles. Zero inverse radius corresponds to bulk silicon. The lines are linear fits of the corresponding set of data. **Right:** 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).

(Left), for both (a) B- and (b) P-doped nanoclusters, as a function of the inverse radius of the system. From Fig. 1(a) (Left) it is seen that for B-doped nanoclusters, for larger systems the substitutional impurity is more stable. For the relaxed bulk system we get a formation energy of 0.8 eV. The solid line is a linear fit to the first set of the data ($E_f = 2.07325 + 5.40348/R$, where R is expressed in \AA and E_f in eV) while the dashed line a linear fit for the third set of the data ($E_f = 0.796 + 4.63971/R$). The second set of data shows negligible variations with respect to the first one. For P-doped nanoclusters the same decreasing behaviour of ΔE_f is observed, as shown in Fig. 1(b) (Left). The solid line is, again, a linear fit of the first set of data ($E_f = 0.21008 + 4.98131/R$).

It can be interesting to see how the formation energy changes as a function of the impurity position within the cluster. In Fig. 1 (Right) we show the formation energy for the B neutral impurity in the $\text{Si}_{146}\text{BH}_{100}$ cluster.

The impurity is moved from the cluster centre toward the surface along two paths, shown in Fig. 1(a) (Right). The calculated energies are shown in Fig. 1(b) (Right). On the x -axis we put the distance from the centre of the replaced Si atom in the $\text{Si}_{147}\text{H}_{100}$ 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 or 0.35 eV is found as the B is moved to the Si layer just below the surface. Thus, as the B atom is moved toward the surface the formation energy decreases, making the positions underlying the surface more stable. The impurity activation energy is calculated using the formula [3]

$$E_{\text{act}}(B) = I_u - A_d; E_{\text{act}}(P) = I_d - A_u, \quad (2)$$

where $I = E(n-1) - E(n)$ and $A = E(n) - E(n+1)$ give the nanocluster ionisation energy and electron affinity respectively, while the subscripts u and d refer to the pure (undoped) and doped system respectively. The results for I_u and A_u are in fair agreement with those of refs. [3]. A linear scaling of E_{act} 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 [4]. The linear fit provides E_{act} for any nanocrystal dimension. We obtain: $E_{\text{act}} = 0.050904 + \frac{16.298819}{R}$, where R has to be expressed in \AA and E_{act} in eV.

Coming to the B and P co-doped Si-nc [5], it is interesting to note that in the co-doped case the differences among the four impurity-Si bond lengths around the impurities are smaller with respect to the single-doped case (the Si-B bonds differ of about 1.08% in the single-doped case and only 0.64% in the co-doped case, whereas this variation in the case of P reduces from 3.61% to 1.54%). Thus, if carriers in the Si-nc are perfectly compensated by simultaneously doping 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 has a profound influence on the FE of the impurities. The FE's, as calculated from Eq. (1), are reported in Fig. 2 (Left), for B-, P-doped and B-P-co-doped Si-nc for the two considered cases. From Fig. 2 it is clear that simultaneous doping strongly reduces (of about 1 eV) ΔE_f with respect to both single-doped cases. This reduction is similar for Si-nc of different size. The important point here is that Si-nc can be more easily simultaneously doped than single-doped; this is a consequence of both the charge compensation and the minor structural deformation. Doping plays also an important role regarding the electronic properties of Si-nc. Fig. 2 (Right) shows the energy levels at the Γ point for $\text{Si}_{87}\text{H}_{76}$, $\text{Si}_{86}\text{BH}_{76}$, $\text{Si}_{86}\text{PH}_{76}$, and $\text{Si}_{85}\text{BPH}_{76}$ calculated at the optimized geometries. In Fig. 2 (Right) only the levels corresponding to the HOMO, LUMO, HOMO-1 and LUMO+1 states are showed. Fig. 3 visualizes the calculated square modulus contour plots related to HOMO and

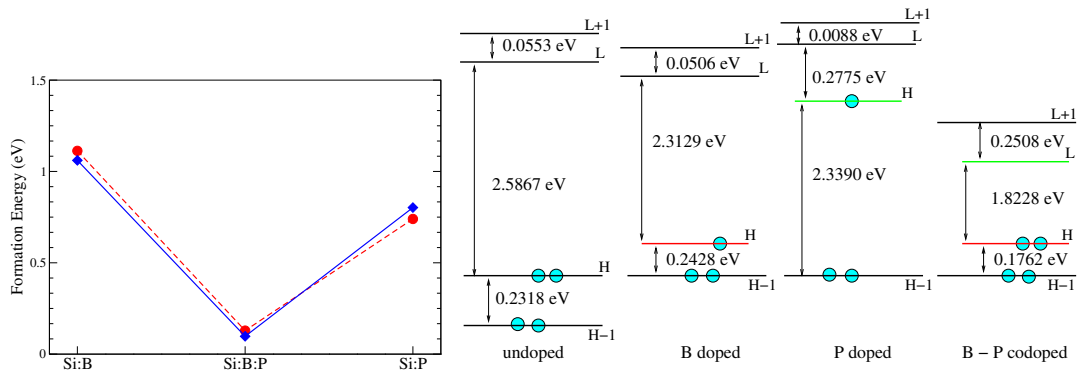


FIG. 2: **Left:** Formation energy of the neutral impurities, as a function of the doping. B and P single-doped and B-P co-doped nanoclusters are considered. The lines are a guide for the eyes. Solid (blue) line is related to the $\text{Si}_{87}\text{H}_{76}$ nanoclusters, dashed (red) line to the $\text{Si}_{147}\text{H}_{100}$ ones. **Right:** Calculated energy levels at Γ point for the $\text{Si}_{87}\text{H}_{76}$, $\text{Si}_{86}\text{BH}_{76}$, $\text{Si}_{86}\text{PH}_{76}$ and $\text{Si}_{85}\text{BPH}_{76}$ -nc.

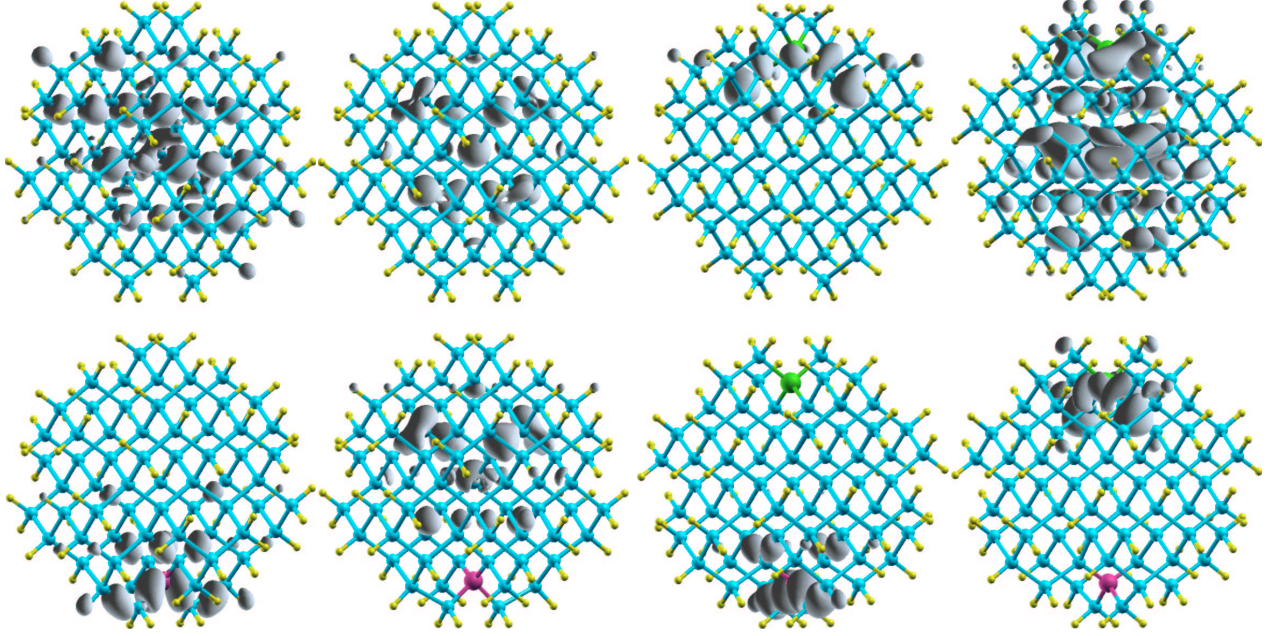


FIG. 3: HOMO (left) and LUMO (right) square modulus contour plots calculated for the $Si_{87}H_{76}$ (**Top Left**), $Si_{86}BH_{76}$ (**Bottom Left**), $Si_{86}PH_{76}$ (**Top Right**) and $Si_{85}BPH_{76}$ (**Bottom Right**) nanoclusters. The isosurfaces correspond to 10% of the maximum value. B (violet) impurity is located at the bottom of the Si-nc, P (green) at the top.

LUMO states, showing their localization within the Si-nc. From these figures it is evident how the changes in the electronic properties of the Si-nc are directly related to the impurities valence. The presence of donor or acceptor states lowers the energy gap (E_G). For single-doped Si-nc the HOMO level now contains only one electron and is localized either on B or P impurity. The electronic properties of B- and P- co-doped Si-nc are qualitatively and quantitatively different from those of either B- or P- doped Si-nc. E_G is lowered from 2.5867 eV (pure Si-nc) to 1.8228 eV (co-doped Si-nc). The results for the $Si_{147}H_{100}$ case are similar: E_G reduces from 2.2975 eV of the pure Si-nc to 1.5560 eV of the $Si_{145}BPH_{100}$ nanocrystal. For pure Si-nc larger than those considered here, having a smaller E_G , it would be possible by co-doping to obtain an E_G even smaller than the bulk Si band gap. Moreover looking at the HOMO and LUMO contour plots we see that these states progressively localize on the impurities on going from the pure to the co-doped Si-nc. Thus, one can expect for the exciton an enhancement of the intensity as consequence of the localization process. These outcomes can explain the data of Fujii et al. [6], which have observed a PL intensity for co-doped Si-nc even higher than that of pure Si-nc and have showed that by co-doping it is possible to shift the PL peak below the bulk band gap.

In conclusion, we have reported on a detailed first-principle calculation of the impurity states in B- and P- single- and co-doped Si-nc. The FE have been discussed as a function of both the size and the position within the Si-nc. Moving the impurity from the cluster centre, the FE gets lower, showing that substitutional positions near the surface are more stable. The activation energy is a decreasing function of the size. In the co-doped systems it has been shown that, as consequence of charge compensation, it is easier to co-dope than to single-dope Si-nc. Moreover study of the electronic properties shows that for the simultaneously B- and P-doped Si-nc both HOMO and LUMO are localized around the impurity sites thus strongly lowering the E_G with respect to that of the pure Si-nc. This fact allows electronic transitions between donor and acceptor states, making it possible to engineer the PL spectrum.

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