Density functional theory study on the B doping and B/P codoping of Si nanocrystals embedded in SiO$_2$

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Doping silicon nanocrystals (Si NCs) embedded in silicon dioxide (SiO$_2$) with boron (B) and phosphorus (P) is a promising way of tuning the properties of Si NCs. Here we take advantage of density functional theory to investigate the dependence of the structural and electronic properties of Si NCs embedded in SiO$_2$ on the doping of B and P. The locations and energy-level schemes are examined for singularly B-doped or B/P-codoped Si NCs embedded in SiO$_2$ with a perfect or defective Si/SiO$_2$ interface at which a Si dangling bond exists. A dangling bond plays an important role in the doping of Si NCs with B or B/P. The doping behavior of B in Si NCs embedded in SiO$_2$ vastly differs from that of P. The electronic structure of a B/P-codoped Si NC largely depends on the distribution of the dopants in the NC.

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I. INTRODUCTION

Silicon nanocrystals (Si NCs) have been intensively investigated during past decades for their promising applications in various fields such as optoelectronics [1–6], photovoltaics [7–11], energy storage [12,13], and bioimaging [14,15]. This is mainly due to their nontoxicity, low cost, and compatibility with well-established Si-based microelectronic technology. It has been recently shown that doping is a critical means to realize the full potential of Si NCs [16–19]. For example, low-energy light emission related to the transitions of electrons from the band edge to the defect state has been observed in boron (B)- and phosphorus (P)-doped Si NCs [20–23], leading to enhanced tunability of the light emission from Si NCs. In addition, heavy B and P doping have enabled localized surface plasmon resonance (LSPR) for Si NCs [24–28]. A series of novel devices that take advantage of the doping-induced properties of Si NCs are now highly expected. Among a variety of matrices in which Si NCs can be embedded, SiO$_2$ is very popular because of the excellent availability of SiO$_2$ and the high-quality interface between Si NCs and SiO$_2$ [29–31]. Therefore, the doping of Si NCs embedded in SiO$_2$ deserves careful investigation during the course of advancing Si-NC-based technology.

In contrast to the doping of hydrogen-passivated Si NCs, the doping of Si NCs embedded in SiO$_2$ has not been systematically simulated because complicated models need to be used in the simulation [32–35]. Guerra and Ossicini [36] and Carvalho et al. [37] investigated the doping of B and P in Si NCs that were passivated by OH groups. However, the absence of the Si/SiO$_2$ interface in their OH-terminated Si NC models was somehow far away from the routinely encountered situation. We have recently managed to simulate the P doping of Si NCs embedded in SiO$_2$ by constructing SiO$_2$-coated Si NCs [38]. The results highlighted the difference in the distribution of P and the electronic properties between hydrogen-passivated Si NCs and those with oxide at the surface [38,39]. Now we further investigate the B doping and B/P codoping of Si NCs embedded in SiO$_2$ in the framework of density functional theory (DFT). The model of a Si NC embedded in SiO$_2$ (Si@SiO$_2$) is constructed by coating a 1.4-nm Si NC with a monolayer of SiO$_2$ (0.25 nm thick), which is itself passivated by hydrogen. It has been already demonstrated that the rather thin SiO$_2$ layer is able to model the matrix-induced strain as well as the defective Si/SiO$_2$ interface [38,40]. For all NC models that are constructed this way, a full geometry optimization is performed. The locations and energy-level schemes are examined for B-doped or B/P-codoped Si NCs embedded in SiO$_2$ with a perfect or defective Si/SiO$_2$ interface. It is found that the B doping vastly differs from the P doping for Si NCs embedded in SiO$_2$. We also show that the electronic structures of B/P-codoped Si NCs embedded in SiO$_2$ are closely related to the distribution of the dopants.

II. METHOD

The optimization of structures and the calculation of total energies are performed at 0 K by using the all-electron DFT modeling package DMol3 [38,41,42]. The Becke-Lee-Yang-Parr (BLYP) exchange-correlation functional at the generalized gradient approximation (GGA) level is used. Double numerical basis sets augmented with p-polarization functions (DNP basis sets) are employed as the atomic orbital basis functions. To ensure accurate calculation, a high self-consistent field (SCF) convergence threshold of $10^{-5}$ and a large orbital cutoff of 4.6 Å are employed. The maximum energy change and forces on all of the atoms in the optimized structures are less than $10^{-5}$ Ha and 0.002 Ha/Å, respectively. To prevent the optimizer from taking unreasonable steps, the maximum allowed change of any Cartesian coordinate during the structural relaxation is less than 0.3 Å. The highest occupied molecular orbital (HOMO), highest occupied deep energy level (HODE), lowest unoccupied deep energy level (LUDE), and lowest unoccupied molecular orbital (LUMO) are sampled on a grid with a spacing of 0.2 Å.
The formation energies of dangling bonds with these three configurations. It turns out that when a B atom replaces a Si atom that is originally connected to one, two, or three H atoms at the surface of Si@SiO$_2$ or Si@$_{db}$SiO$_2$, it is denoted as $B_a$, $B_b$, or $B_c$, respectively. $B_a$, $B_b$, and $B_c$ are passivated by zero, one, and zero H atoms, respectively. As a B atom passivates a Si dangling bond at the Si/SiO$_2$ interface, it is denoted as $B_{db}$.

III. B DOPING

A. Formation energy

Figure 1 shows the model of a geometry-optimized 1.4-nm Si NC embedded in SiO$_2$ with (a) a perfect Si@SiO$_2$ interface (Si@SiO$_2$, $Si_{123}H_{100}O_{96}$) or (b) defective Si@SiO$_2$ interface at which a Si dangling bond exists (Si$_{a,db}$SiO$_2$, $Si_{123}H_{100}O_{96}$). Si, H, and O atoms are denoted by green, gray, and red balls, respectively. A Si atom initially with a dangling bond at the Si/SiO$_2$ interface is highlighted by an orange ball. A substitutional or passivating B atom is indicated by a violet ball. B$_1$, B$_2$, B$_3$ (B$_3$), B$_4$ (B$_4'$), and B$_5$ (B$_5'$) result from moving a substitutional B atom along the path of $1 \rightarrow 2 \rightarrow 3$ (3') $\rightarrow 4$ (4') $\rightarrow 5$ (5'). When a B atom replaces a Si atom connected to one, two, or three H atoms at the surface, it is denoted as $B_a$, $B_b$, or $B_c$, respectively. As a B atom passivates a Si dangling bond at the Si/SiO$_2$ interface, it is denoted as $B_{db}$.

We have calculated the formation energy ($E_f$) of a B atom in Si@SiO$_2$ or Si@$_{db}$SiO$_2$ by using [50,51]

$$E_f = E(Si_{x,y,z}H_3\_B) - E(Si_{x,y,z}H_3) - \mu_B - (x' - x)\mu_{Si} - (y' - y)\mu_O - (z' - z)\mu_H,$$

where $E(Si_{x,y,z}H_3\_B)$ and $E(Si_{x,y,z}H_3\_B)$ are the total energy of Si@SiO$_2$ or Si@$_{db}$SiO$_2$ before and after the incorporation of a B atom, respectively. $x, x'$, $y, y'$, and $z, z'$ are the numbers of Si, O, and H atoms, respectively. $\mu_{Si}, \mu_O, \mu_H$, and $\mu_B$ are the chemical potentials of Si, O, H, and B, respectively. The relative order of $E_f$ for B in all kinds of configurations is not affected by the chemical potentials in a rather wide range given the linear relationship between $E_f$ and each chemical potential. Thus we obtain the values of $E_f$ by choosing $\mu_{Si}, \mu_O, \mu_H$, and $\mu_B$ to equal the total energies of atomic Si, O, H, and B in bulk Si, oxygen gas, hydrogen gas, and B$_{12}$, respectively [52,53].

Figure 2 shows the values of $E_f$ with respect to the location of B in (a) Si@SiO$_2$ or (b) Si@$_{db}$SiO$_2$. It is seen that the values of $E_f$ for B at the Si/SiO$_2$ interface and the surface of Si@SiO$_2$ [i.e., the locations of 4 (4'), 5 (5'), $a$ and $b$] are close to those for B in the NC core [Fig. 2(a)]. This result is quite different from that for P-doped Si@SiO$_2$, in which a P atom in the core shows a lower $E_f$ than that for B in the NC core [38]. Such a difference may be due to the fact that the electronegativity of B is weaker than that of P. Attractive interaction between B and O is larger than that between P and O. The minimum value of $E_f$ (−5.6 eV) appears when B is incorporated as B$_3$' in the subinterface region, indicating that B is the most likely doped at the subinterface region. This is in contrast to the doping of Si@H with B, where B prefers residing at the surface of Si@H [54].

Figure 2(b) shows the dependence of $E_f$ on the location of B for Si@$_{db}$SiO$_2$. It is noticed that the value of $E_f$ for B$_5$ at the Si/SiO$_2$ interface is the lowest (−6.1 eV), implying that the Si/SiO$_2$ interface is more energetically favored for B.
when a dangling bond exists at the Si/SiO₂ interface. Since dangling bonds often exist at the Si/SiO₂ interface in the real world [55], our current result predicts that B may be routinely found to preferentially occupy the Si/SiO₂ interface region when a Si NC embedded in SiO₂ is doped with B. Khelifi et al. [56] and Xie et al. [57] have recently demonstrated that this is indeed the case. The existence of a dangling bond at the Si/SiO₂ interface also reduces the values of $E_f$ for B in the NC core [Fig. 2(b)], which means that defects such as Si dangling bonds at the Si/SiO₂ interface may facilitate the incorporation of B for Si NCs embedded in SiO₂. In contrast to P-doped Si@$_{db}$SiO₂ [38], B is the least likely to passivate dangling bonds in Si@$_{db}$SiO₂. This is consistent with Fujio et al.’s [55] experimental work on B-doped Si NCs embedded in SiO₂. They showed that the electron spin resonance (ESR) signal of dangling bonds remains after Si NCs are doped with B.

**B. Electronic structure**

Figure 3 shows the energy-level diagrams for undoped and B-doped (a) Si@SiO₂ or (b) Si@$_{db}$SiO₂. For Si@SiO₂, deep energy levels are introduced in the band gap when B is in the configurations of B1, B2, B3 (B’3), B4 (B’4), and B5 (B’5). This is mainly due to the B-doping-induced odd number of electrons in a NC. Among these configurations, the B-doping-induced deep energy levels of B1, B2, B3, and B’3 are close to the valence band with a small spin splitting, while those of B4, B4’, B5, and B’5 are deep with a large spin splitting. The spin splitting of the deep energy level is associated with the polarizability of bonds, which is determined by the variation of the bond length. For B-doped Si@SiO₂ with the configurations of B1, B2, B3, and B’3, the bond lengths of four Si-B bonds are almost identical with each other, giving rise to rather small polarization of the bonds. In these cases, the electron density of the HODE and LUDE are mainly located at the B and neighboring Si atoms with similar distributions [representatively shown for Si@SiO₂ doped with B’3 in Fig. 4(a)]. However, there are significant changes of bond length when B is doped in the configurations of B4, B4’, B5, and B’5. For example, for B-doped Si@SiO₂ with the configuration of B5, the bond length of a Si-B bond is stretched by 60% and that of the adjacent Si-B bond is compressed by 10%. For B’5-doped Si@SiO₂, the B atom even moves to the NC surface after structural optimization [Fig. 1(a)], creating a Si dangling bond at the Si/SiO₂ interface. In these cases, the electron density of the HODE and LUDE are mainly localized at the B atom and adjacent Si dangling bond with divergent distributions [representatively shown for Si@SiO₂ doped with B5 in Fig. 4(a)]. It is the strong localization and divergent distribution of the electron density of HODE and LUDE that contributes to the deep energy levels and large spin splitting, respectively.

The band gap of undoped Si@SiO₂ is slightly enlarged when a dangling bond exists at the Si/SiO₂ interface (1.59 → 1.66 eV). In the meantime, the dangling bond introduces deep energy levels in the band gap, which is evidenced by the fact that the electron density of the HODE and LUDE of Si@$_{db}$SiO₂ are mainly localized at the dangling bond [Fig. 4(b)]. For Si@$_{db}$SiO₂ doped with B in the configurations of B1, B2, B3 (B’3), B4 (B’4), and B5 (B’5), deep energy levels remain. Similar to what happens to Si@SiO₂, the bond length is almost unchanged when B is doped in the configurations of B1, B2, B3, and B’3. The electron density of the HODE are localized around B, while those of the LUDE are localized on the dangling bond [representatively shown for Si@$_{db}$SiO₂ doped with B’3 in Fig. 4(b)]. We find that the single electron of the original dangling bond is transferred to form an electron pair together with that of a B atom. The electron pair occupies the HODE with opposite spins, consistent with Pauli’s exclusion principle. For the configurations of B4, B4’, B5, and B’5, significant changes of bond length appear. Both the electron density of the HODE and LUDE are localized on the dangling bond and the Si atom with the largest bond length, leading to deeper energy levels in the band gaps of these configurations. In contrast to P-doped Si@$_{db}$SiO₂ with the configuration of P$_{db}$ [38], B doping does not eliminate the deep energy levels with the configuration of B$_{db}$ [Fig. 3(b)]. The electron density of the HODE and LUDE are mainly localized on B$_{db}$ [Fig. 4(b)]. The incorporation of Bₐ, Bₜ, or Bₕ hardly changes the energy-level scheme and electron density of the HOMO and LUMO for Si@SiO₂ or Si@$_{db}$SiO₂ (Figs. 3 and 4) because Bₐ, Bₜ, or Bₕ is in threefold coordination at the surface without introducing a single electron.

**FIG. 3.** Energy-level diagrams for undoped and B-doped (a) Si@SiO₂ or (b) Si@$_{db}$SiO₂ at the ground state. Filled (empty) circles indicate that energy levels are occupied (unoccupied) by electrons. Spin-up (spin-down) states of defect energy levels induced by a B atom or dangling bond are indicated by up (down) arrows.
FIG. 4. (a) Distribution of the isosurface for the electron density of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for undoped or B\textsubscript{b}-doped Si@SiO\textsubscript{2}. Those of the highest occupied deep energy-level (HODE) and the lowest unoccupied deep energy-level (LUDE) for B\textsubscript{3\textsuperscript{\prime}}- or B\textsubscript{5}-doped Si@SiO\textsubscript{2} are also shown. (b) Distribution of the isosurface for the electron density of the HODE and LUDE for undoped, B\textsubscript{3\textsuperscript{\prime}}-, B\textsubscript{5}-, or B\textsubscript{db}-doped Si@\textsubscript{db} SiO\textsubscript{2}.

IV. B/P CODOPING

A. Formation energy

Now we focus on the synergic effect of B/P codoping for Si NCs embedded in SiO\textsubscript{2}. For Si@SiO\textsubscript{2}, the configurations in which B and P are both incorporated in their energetically favored locations of 3 (3\textsuperscript{\prime}) at the subinterface region of the NC are first considered \cite{38}. For these configurations, the dopants can either be located separately (denoted as P3-B3\textsuperscript{\prime}) or form a B-P pair (denoted as {P3-B3\textsuperscript{\prime}} or {P3\textsuperscript{\prime}-B3}). In order to figure out which atom is more likely to be incorporated into the core region of the NC when it is codoped with B and P, the configuration of P1-B3\textsuperscript{\prime} or P3\textsuperscript{\prime}-B1 with a P or B atom in the center of the NC is representatively considered. For Si@\textsubscript{db}SiO\textsubscript{2}, given the result that P is the most likely to passivate the dangling bond at the Si/SiO\textsubscript{2} interface \cite{38}, the dangling bond is first passivated by a P atom. A substitutional B atom moving along the path of 1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 is considered. To avoid any strong interaction between the dopants, the path is chosen to be far from P\textsubscript{db}. These configurations are denoted as P\textsubscript{db}-B1, P\textsubscript{db}-B2, P\textsubscript{db}-B3, P\textsubscript{db}-B4, and P\textsubscript{db}-B5. Moreover, a B-P pair in the configuration of {P\textsubscript{db}-B4\textsuperscript{\prime}} is considered to investigate the interaction between the dopants for Si@\textsubscript{db}SiO\textsubscript{2}. Figure 5 shows the models of (a) P3-B3\textsuperscript{\prime} codoped Si@SiO\textsubscript{2} and (b) P\textsubscript{db}-B5 codoped Si@\textsubscript{db}SiO\textsubscript{2}.

The $E_f$ of the dopants in Si@SiO\textsubscript{2} or Si@\textsubscript{db}SiO\textsubscript{2} is calculated by using

$$E_f = E(Si_xO_yH_zBP) - E(Si_xO_yH_z) - \mu_B - \mu_P - (x' - x)\mu_{Si} - (y' - y)\mu_{O} - (z' - z)\mu_{H}. \quad (2)$$

$E(Si_xO_yH_z)$ and $E(Si_xO_yH_zBP)$ are the total energy of Si@SiO\textsubscript{2} or Si@\textsubscript{db}SiO\textsubscript{2} before and after the incorporation of B/P dopants, respectively. $x (x')$, $y (y')$, and $z (z')$ are the numbers of Si, O, and H atoms, respectively. $\mu_P$ is the chemical potential.

FIG. 5. Model of a (a) Si@SiO\textsubscript{2} codoped with P3 and B3\textsuperscript{\prime} or (b) Si@\textsubscript{db}SiO\textsubscript{2} codoped with P\textsubscript{db} and B5. Si, H, O, B, and P atoms are denoted by green, gray, red, violet, and blue balls, respectively.
FIG. 6. Formation energies of B/P dopants in (a) Si@SiO2 or (b) Si@\textsubscript{db}SiO2.

FIG. 7. Energy-level diagrams for undoped and B/P-codoped (a) Si@SiO2 or (b) Si@\textsubscript{db}SiO2 at the ground state. Filled (empty) circles indicate that energy levels are occupied (unoccupied) by electrons. Spin-up (spin-down) states of defect energy levels are indicated by up (down) arrows. The highest occupied deep energy-level (HODE) and lowest unoccupied deep energy-level (LUDE) are indicated by red bars.

B. Electronic structure

The energy-level diagrams for undoped and B/P-codoped Si@SiO2 or Si@\textsubscript{db}SiO2 are shown in Fig. 7. For Si@SiO2, deep energy levels are introduced in the band gap when B and P are in the configurations of P1-B3', P3-B3', and P3'-B1. The electron density of HODE and LUDE are mainly localized at B and P, respectively. This is representatively shown for Si@SiO2 codoped with P1-B3' or P3-B3' in Fig. 8(a). Figure 9 shows the HODE-LUDE, LUDE-LUMO, and HODE-HOMO gaps for B/P-codoped Si@SiO2 with the configuration of P1-B3', P3-B3', or P3'-B1. It is seen that the band gap between the deep energy levels (HODE-LUDE gap) varies from 1.0 to 1.5 eV for B/P-codoped Si@SiO2 within these configurations. The LUDE-LUMO gap is much larger than the HODE-HOMO gap for the configurations of P1-B3', P3-B3', and P3'-B1. This demonstrates that the depth of B/P-codoping-induced energy levels is affected by the relative
FIG. 8. (a) Distribution of isosurface for the electron density of the HODE and LUDE for P1-B3′ or P3-B3′ codoped Si@SiO2. Those of the HOMO and LUMO for {P3-B3′} codoped Si@SiO2 are also shown. (b) Distribution of the isosurface for the electron density of the HODE and LUDE for P_{db}-B3 or P_{db}-B5 codoped Si@_{db}SiO2.

positions of B and P atoms in the NC. Recently, Nakamura et al. [31] observed multiphotoluminescence (PL) peaks in heavily B/P-codoped Si NCs embedded in SiO2. The PL energy of one of the peaks depends on the dopant concentration. These experimental results can be well explained by our current finding that B/P codoping leads to localized states with different depths in the band gap, which are responsible for different PL energies. When B and P atoms are codoped in the form of B-P pairs (i.e., {P3-B3′} and {P3′-B3}), no deep energy levels are introduced in the band gap. The electron density of the HOMO and LUMO are basically delocalized among Si atoms [representatively shown for Si@SiO2 codoped with {P3-B3′} in Fig. 8(a)].

For Si@_{db}SiO2, when a P atom passivates the dangling bond with the configuration of P_{db}, the energy-level scheme of the NC becomes akin to that of undoped Si@SiO2 [38]. Similar to what happens to Si@SiO2, the incorporation of an additional B atom in the configurations of B1, B2, B3, B4, and B5 introduces deep energy levels in the band gap of Si@_{db}SiO2. For B/P-codoped Si@_{db}SiO2 with the configurations of P_{db}-B1, P_{db}-B2, P_{db}-B3, P_{db}-B4, and {P_{db}-B4′}, the electron density of the HODE and LUMO are mainly localized at the B atom [representatively shown for Si@_{db}SiO2 codoped with P_{db}-B3 in Fig. 8(b)]. For P_{db}-B5 codoped Si@_{db}SiO2, significant changes of bond length appear. The electron density of the HODE and LUMO are mainly localized at the B and Si atoms with the largest structural distortion [Fig. 8(b)].

V. CONCLUSIONS

We have studied the B doping and B/P codoping of a Si NC embedded in SiO2 with a perfect Si/SiO2 interface (Si@SiO2) or defective Si/SiO2 interface (Si@_{db}SiO2). The current results show that B is most likely incorporated into the subinterface of Si@SiO2. However, the existence of a dangling bond at the Si/SiO2 interface makes B more energetically prefer the Si@SiO2 interface. In contrast to the doping of Si@_{db}SiO2 with P, B is not likely to passivate the dangling bond.

For B/P-codoped Si@SiO2, a B atom and a P atom tend to be bonded as a B-P pair at the subinterface of the NC. A larger electronic attractive interaction between B and O atoms makes B atoms more energetically prefer positions close to the SiO2 layer. As a consequence, a static electric dipole that radially points toward the NC core is formed at the subinterface region. In fact, B or P may enter the NC core when they are heavily doped. In this case, deep energy levels are introduced in the band gap of Si@SiO2. The HODE-LUDE gap is affected by the relative positions of B and P atoms.
Finally, we would like to comment on the dependence of the properties of B-doped and B/P-codoped Si NCs embedded in SiO$_2$ on the NC size. As previously demonstrated for P-doped Si NCs embedded in SiO$_2$ [38], the trend of the variation of $E_f$ with respect to the dopant atom position may not change despite the change of the specific value of $E_f$ when the NC size varies. Therefore, the similar preferential distribution of B and codoped B/P should occur as the NC size changes despite the change of the specific value of $E_f$ providing computation resources. This study is mainly supported by the National Basic Research Program of China (Grant No. 2013CB632101), the Natural Science Foundation of China (NSFC) for Excellent Young Researchers program (Grant No. 61222404), and the NSFC-FWO program (Grants No. 61411130229 and No. 6151110264).

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