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Chemical trends of defect formation in Si quantum dots: The case of group-III and group-V dopants

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Using first-principles methods, we have systematically calculated the defect formation energies and transition energy levels of group-III and group-V impurities doped in H passivated Si quantum dots (QDs) as functions of the QD size. The general chemical trends found in the QDs are similar to that found in bulk Si. We show that defect formation energy and transition energy level increase when the size of the QD decreases; thus, doping in small Si QDs becomes more difficult. B_{Si} has the lowest acceptor transition energy level, and it is more stable near the surface than at the center of the H passivated Si QD. On the other hand, P_{Si} has the smallest donor ionization energy, and it prefers to stay at the interior of the H passivated Si QD. We explained the general chemical trends and the dependence on the QD size in terms of the atomic chemical potentials and quantum confinement effects.

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I. INTRODUCTION

The application of semiconductors as novel electrical and optical devices requires that the materials can be doped so that enough charge carriers can be generated in a controllable manner at working temperature.[1–3] Si is one of the most favored materials for microelectronic application industry because it is abundant, can be grown in very high-quality single crystals, and can be doped relatively easily both in *p* and *n* types. The size of the Si-based electronic devices has been decreasing steadily and rapidly, approaching the nanometric dimensions. As for many other physical properties, when the size of Si reaches the nanolimit, due to the quantum confinement effects, the doping properties of Si quantum dots (QDs) could be significantly different from that in bulk Si. Moreover, to make the device functioning at this reduced size, higher carrier density is often needed.[4] Despite the fact that extensive studies have been carried out in the past to understand and improve doping properties in bulk semiconductors,[5,6] very little is know about the doping properties in nanosized semiconductors.[7–16] It has been found that the electrical conductivity of nano or porous Si is very low at room temperature, suggesting low dopability.[11,17] However, the origin of this doping difficulty is not well understood. It is not clear if the reduced dopability is energetic, i.e., the formation energy of the dopants increases in QDs, or kinetic, i.e., the increased surface-to-bulk ratio in QDs makes the defect easier to diffuse out of the QDs. Therefore, it is of great interest to study how the doping properties of Si are affected by the size of the nanocrystals.

In this paper, to understand the doping properties in Si QDs, we have systematically calculated the defect formation energies and transition energy levels of group-III and group-V dopants as a function of the Si QD size using the first-principles band-structure and total-energy methods. Our calculations show that the formation energies and transition energy levels with respect to the band edges increase as the QD size decreases; thus, doping in small Si QDs is expected to be intrinsically more difficult than in big ones, consistent with experimental observations.[11,17] For group-III acceptors, B has relatively small formation energy and transition energy level with respect to the valence-band maximum (VBM), so it is considered as the best acceptor in Si. For group-V donors, P has the lowest transition energy level with respect to the conduction-band minimum (CBM) and a relatively small formation energy, so it is considered as the best donor in Si. This chemical trend is similar to that found in bulk Si and can be explained by the size and atomic chemical potential of the elements. We have also studied the relative stability of the dopants in different sites of the QDs. We find that for H passivated Si QDs, B impurity is more stable near the surface than at the center. On the contrary, P impurity tends to stay at the interior of Si QDs. These results can be explained by combined effects of charge compensation and strain reduction at the QD surfaces.

This paper is organized as follows. Section II describes our calculation method. Section III discusses the chemical trends of the defect formation energies and transition energy levels of group-III and group-V dopants in bulk Si. Section IV discusses the calculated formation energies of these impurities in Si QDs. Section V discusses the transition energy levels of these impurities in Si QDs. Finally, Sec. VI gives a brief summary of the main conclusions of this paper.

II. METHODS OF CALCULATIONS

In this work, the defect formation energies and transition energy levels of group-III and group-V dopants in Si QDs are calculated using the density functional theory within the local-density approximation[18] (LDA) as implemented in the Vienna *ab initio* simulation package (VASP) code.[19] We used the Vanderbilt ultrasoft pseudopotentials.[20] The calculated

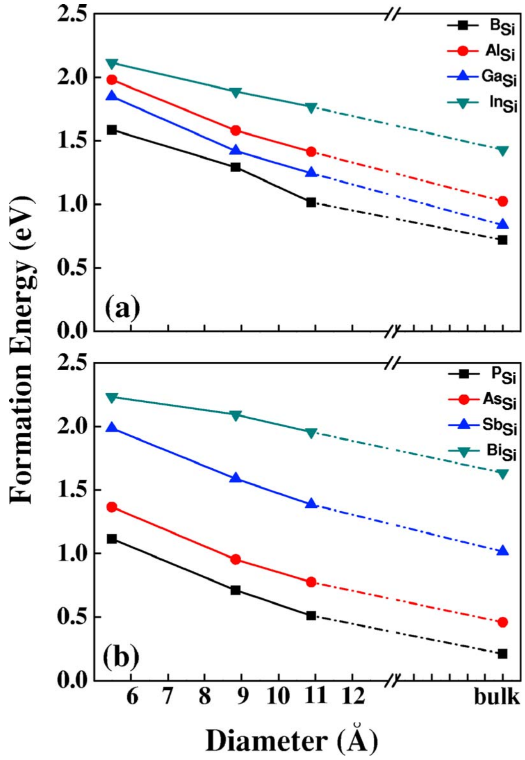

FIG. 1. (Color online) The defect formation energy of (a) group-III acceptors and (b) group-V donors in neutral charge state as a function of QD sizes.

bulk Si lattice constant is 5.399 Å, in good agreement with the experimental value of 5.412 Å.[21] The calculated band gap of bulk Si is 0.59 eV, smaller than the experimental value of 1.1 eV,[21] but is consistent with other calculations based on LDA.[22,23] The Si QD is built by including all atoms within a given radius centered at a Si lattice site. At the surface, atoms with more than two dangling bonds are removed and the remaining surface atom dangling bonds of the QD are passivated by hydrogen. The sizes of the QDs and the number of atoms in each QD are listed in Table I, which are accessible dot sizes in experiments. In Table I, D is the nominal diameter of the Si QD, $D=(3/4\pi\times a_0^3/8\times n)^{1/3}$ (Ref. 26), where a_0 is the bulk lattice constant, n is the total number of Si atoms, and m is the number of H atoms at the surface of the QDs. Periodic boundary condition is used in the calculation where QD is embedded in the lattice site of a large simple cubic cell in order to prevent the interaction between the QDs.[24,25] We used the Γ point for the k-point sampling in the QD calculations. The defect system is modeled by putting a defect at the center of a QD, unless specified otherwise. For charged defects, a uniform charge background is introduced to keep the charge neutrality of the supercell. All atoms in the QDs are fully relaxed by minimizing the total-energy and quantum-mechanical forces. For comparison, the doping of the same impurities in bulk Si has also been calculated using supercells.

TABLE I. The size and atomic number of Si_nH_m QDs in this study.

D (Å)	n	m
5.48	35	36
8.84	147	100
10.89	275	172

TABLE II. The defect formation energies $\Delta H_f(\alpha,0)$ of the neutral group-III acceptor defects in bulk Si with $\mu_i=0$, and the transition energy levels $\epsilon_\alpha(0/-)$ referenced to the VBM. The results are compared with experimental acceptor binding energies ϵ_b (Ref. 28).

	B	Al	Ga	In
$\Delta H_f(\alpha,0)$ (eV)	0.72	1.03	0.84	1.43
$\epsilon_\alpha(0/-)$ (eV)	0.06	0.09	0.10	0.16
ϵ_b (eV)	0.044	0.067	0.072	0.156

To determine the defect formation energy and defect transition energy levels, we calculate the total energy $E(\alpha,q)$ for the system containing the relaxed defect α in charge state q, and the total energy $E(\mathrm{Si})$ for the same QDs in the absence of the defect. We also calculate the total energies of all group-III and group-V elemental solids or gases at their stable phases. From these quantities, the defect formation energy $\Delta H_f(\alpha,q)$ is defined[27] as

$$\Delta H_f(\alpha,q)=\Delta E(\alpha,q)+n_{\mathrm{Si}}\mu_{\mathrm{Si}}+n_\alpha\mu_\alpha+qE_F, \qquad (1)$$

where

$$\Delta E(\alpha,q)=E(\alpha,q)-E(\mathrm{Si})+n_{\mathrm{Si}}\mu_{\mathrm{Si}}^0+n_\alpha\mu_\alpha^0+qE_V. \qquad (2)$$

Here, E_F is Fermi energy of the electrons referenced to VBM of Si, E_V. μ_i is the chemical potential of constituent i referenced to elemental solid or gas with chemical potential μ_i^0. The n's are the numbers of Si and extrinsic defects α, and q is the number of electrons, transferred from the QDs to the reservoirs in forming the defect QDs.[6]

The defect transition energy level $\epsilon_\alpha(q/q')$ is the Fermi energy E_F in Eq. (1) at which the formation energy $\Delta H_f(\alpha,q)$ of defect α in charge state q is equal to that of another charge state q' of the same defect.[6] That is,

$$\epsilon_\alpha(q/q')=[\Delta E(\alpha,q)-\Delta E(\alpha,q')]/(q'-q). \qquad (3)$$

A more detailed discussion on $\Delta H_f(\alpha,q)$ and $\epsilon_\alpha(q/q')$ can be found in Ref. 6.

TABLE III. The defect formation energies $\Delta H_f(\alpha,0)$ of the neutral group-V donor defects in bulk Si with $\mu_i=0$, and the transition energy levels $\epsilon_\alpha(0/+)$ referenced to the CBM. We use the convention that a positive number in $\epsilon_\alpha(0/+)$ means that the level is below the CBM. The results are compared with experimental donor binding energies ϵ_b (Ref. 28).

	P	As	Sb	Bi
$\Delta H_f(\alpha,0)$ (eV)	0.21	0.46	1.02	1.64
$\epsilon_\alpha(0/+)$ (eV)	0.06	0.13	0.09	0.22
ϵ_b (eV)	0.045	0.054	0.043	0.071

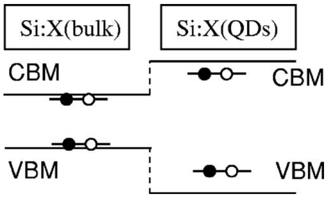

FIG. 2. Schematic illustration of the variation of the single electron energy levels of the defects doped in Si bulk and quantum dots, respectively.

III. FORMATION ENERGIES AND TRANSITION ENERGY LEVELS OF THE DEFECTS IN BULK Si

The defect formation energy $\Delta H_f(\alpha,q)$ of defect α in charge state q determines the dopant solubility in a host at a given growth condition or chemical potentials. High formation energy corresponds to low solubility. Tables II and III list the calculated values of the defect formation energies $\Delta H_f(\alpha,0)$ and transition energy levels of group-III and group-V dopants in bulk Si. These results are calculated by using Eq. (1) in the defect-rich condition, i.e., $\mu_i=0$. Tables II and III also present the calculated transition energy levels $\epsilon_\alpha(0/-)$ and $\epsilon_\alpha(0/+)$, respectively. For the group-III acceptor levels $\epsilon_\alpha(0/-)$, they are referenced to the VBM, i.e., the energy above the VBM, whereas for the group-V donor levels $\epsilon_\alpha(0/+)$, they are referenced to the CBM, i.e., the energy below the CBM. The formation energy of the charged defects can be obtained from the calculated formation energy of the neutral defect, the transition energy level, and Eqs. (1) and (3).

For the group-III acceptors, the defect levels consist of the impurity valence *p* orbitals; thus, atom such as B that has low valence *p* orbital energy also has low acceptor level. The atomic valence *p* orbital energies of Al, Ga, and In are similar. However, because Ga and In have occupied 3*d* and 4*d* orbitals, respectively, due to the increase of the *p*-*d* coupling, the acceptor level of Ga and In is higher than that for Al. Our calculated defect transition energy levels in bulk Si agree well with experimental values.[28]

For the group-V donors, the defect levels consist of the impurity valance *s* orbitals; thus, atoms such as P and Sb that have high valence *s* orbital energies also have shallow donor levels. The As 4*s* orbitals are lower than P 3*s* orbitals because of the incomplete screening of the 3*d* orbitals in As. The Bi atom also has low 6*s* orbital energy due to the large relativistic effect. Therefore, the As and Bi donor levels are relatively deep. N has very low *s* orbital energy due to its strong electronegativity. We find that its donor level is inside the valence band of bulk Si; thus, it is unstable. Our results, in general, agree with the observed chemical trends, but the calculated values are larger than experimental data, possibly due to the small cell size used in the calculation and uncertainty in experimental measurements.[28]

IV. FORMATION ENERGY OF THE DEFECTS IN Si QDs

The calculated defect formation energies of neutral group-III and group-V dopants in Si QDs as functions of the QD diameters are shown in Fig. 1. The general chemical trends are similar to that in bulk Si. We see that in both cases, the defect formation energies of the neutral defects increase as the size of the QDs decreases, which means that the defect solubility in small QDs could be low.

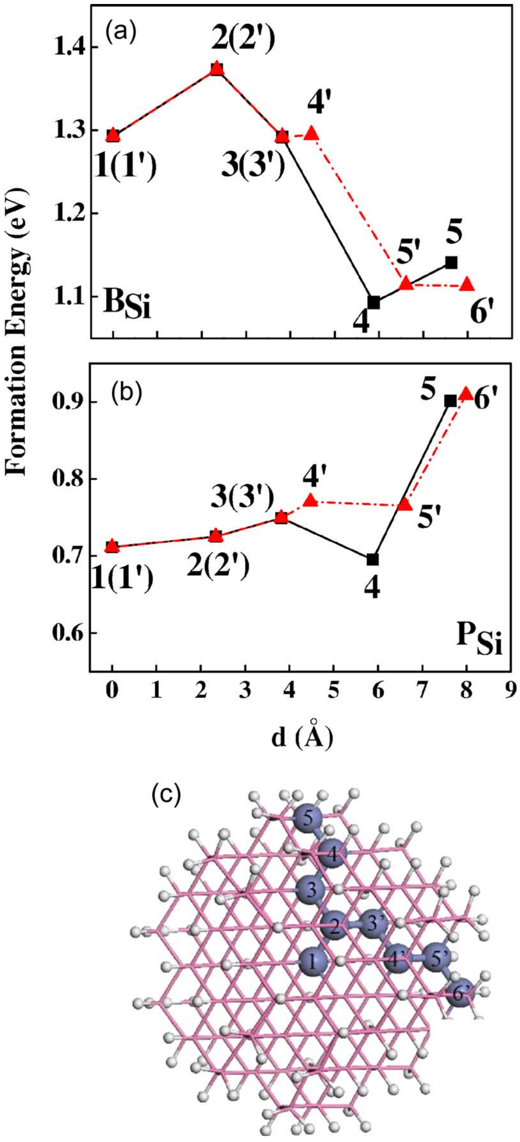

FIG. 3. (Color online) The calculated defect formation energies of (a) B and (b) P impurities at different sites of the Si QD along two different paths as shown in (c).

One of the reasons that the defect formation energy increases with decreasing QD size is because due to the quantum confinement, the antibonding conduction-band energy increases, whereas the bonding valence band decreases.[23] Consequently, the CBM derived donor energy level also increases, whereas the VBM derived acceptor energy level decreases (Fig. 2). Because the neutral donor level is occupied by one electron, the increase of the donor level will lead to an increase of the donor formation energy. On the other hand, the acceptors have one hole at the defect level, and the lowering of the acceptor level (with respect to vacuum) will also lead to an increase of the formation energy. The smaller QDs are also more tightly bonded with smaller Si–Si bond

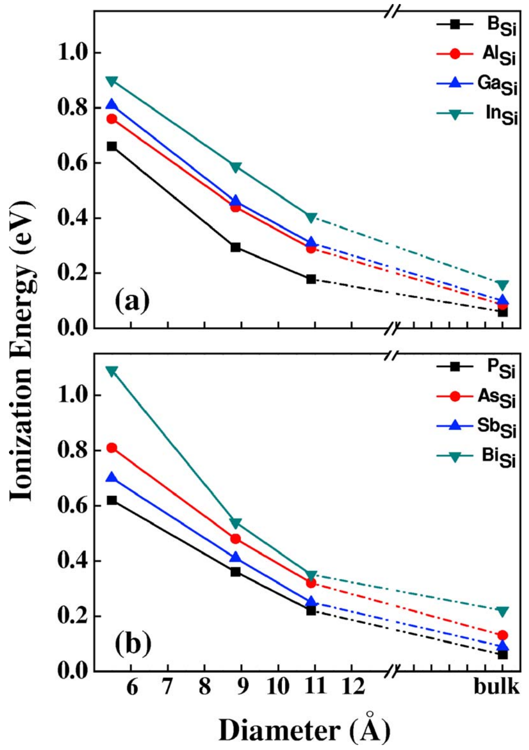

FIG. 4. (Color online) The defect ionization energy levels of (a) group-III acceptor levels referenced to the VBM and (b) group-V donors referenced to the CBM in Si QDs as a function of the QD diameter.

lengths, so the strain effect is also larger in smaller QDs.

We have also studied the stable position of the impurity in the H passivated Si QDs. We calculated the defect formation energies of B and P impurities at different sites of the $Si_{146}X_1H_{100}$ QD along two different paths as shown in Fig. 3(c). Figures 3(a) and 3(b) present the calculated results for B and P dopings, respectively. We find that when the impurity moves away from the center of the QDs toward the surface, the initial variation of the formation energies is small because the local environment around the defect is similar. However, when the impurity reaches the surface at site 5, 5′, and 6′, there are big and nonmonotonic changes in the formation energy. This is because the defect has lower strain energy near the surface than in the interior but has higher chemical energy at the surface sites because the defect is not fully passivated by H atoms at the surface. The variation near the surface reflects the competition between these two effects. For B-doped Si QDs, the defect formation energy, in general, decreases toward the surface [Fig. 3(a)], because B is much smaller than Si; therefore, the strain effect dominates, and the formation energy at the surface is smaller than at the center.[15,22] One the other hand, the defect formation energies for P-doped Si QDs increase toward the surface sites [Fig. 3(b)]. This is because P has nearly the same atomic size as Si, so the strain effect is small. At the surface site, P dangling bond is not fully passivated, so its formation energy becomes larger. Moreover, we find that H is slightly more electronegative than Si, so the Si–H bond at the surface is slightly polarized. The residual Coulomb interaction between the impurity and H also has the effect on the relative stability of impurities. Our discussions above suggest that the relative stability of the defects could depend strongly on the passivating medium at the surface,[13] which could be used as an approach for defect engineering.

V. DEFECT TRANSITION ENERGY LEVELS OF GROUP-III AND GROUP-V DOPANTS IN Si

Group-III elements have one less valence electrons than Si; thus, they form acceptor state near VBM in host Si. On the other hand, group-V elements have one more valence electron than Si; thus, they form donor state near CBM in host Si. Figure 4 depicts the calculated defect ionization energy levels of group-III acceptors and group-V donors in Si QDs as a function of the QD diameters. For comparison, the ionization energy in bulk Si is also presented. In these figures, the hole binding energy for group-III acceptors is with respect to the VBM and the electron binding energy for group-V donors is with respect to CBM.

We see that the general chemical trend is similar as in bulk Si. For the group-III acceptors, the transition energy levels (0/−) of B are the most shallow ones and become more deep from Al impurity to Ga to In impurities. For group-V donors, the transition energy levels (0/+) are shal-

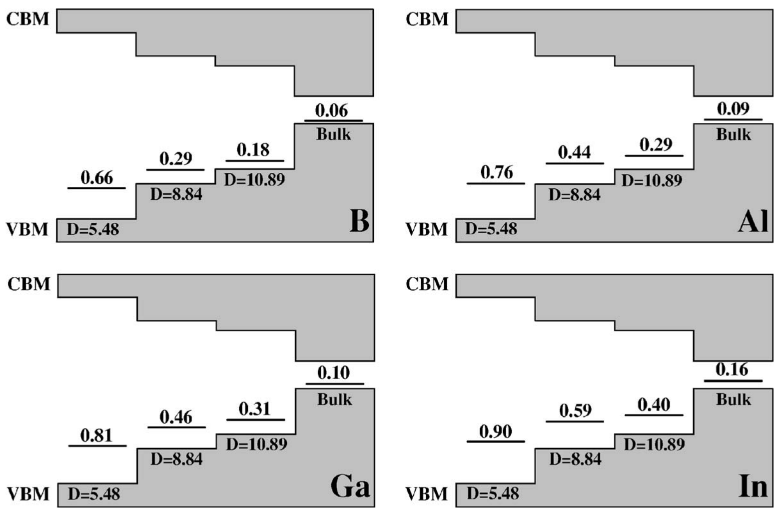

FIG. 5. The absolute defect transition energy level of group-III acceptors in Si QDs. The numbers on the defect levels are the binding energies with respect to the VBM. The QD size is in Å.

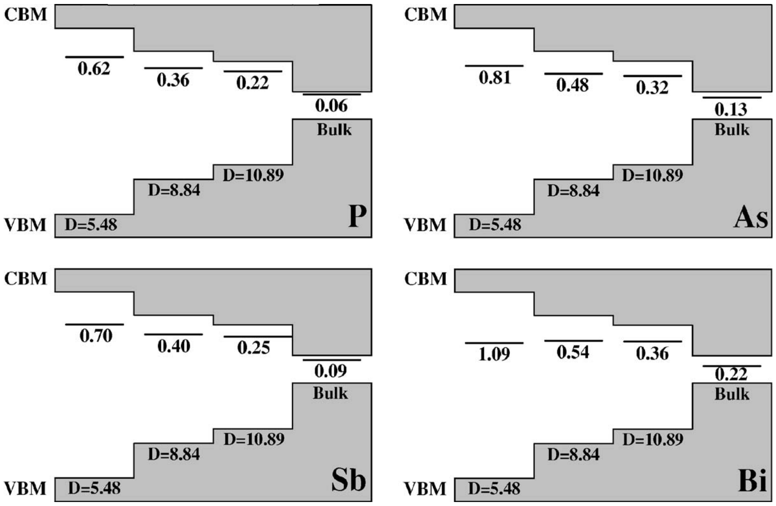

FIG. 6. The absolute defect transition energy level of group-V donors in Si QDs. The numbers on the defect levels are the binding energies with respect to the CBM. The QD size is in Å.

lower for P and Sb dopants but are relatively deep for As and Bi. As the diameter of Si QDs decreases, the transition energy level becomes deeper. This could be understood as follows: When the size of the QDs decreases, quantum confinement moves the CBM upward and the VBM downward. Consequently, the single electron energy level of the defects shifts in the same directions (Fig. 2). However, for the donor states, because they mixed some VBM *p* characters into their wave functions due to the reduced symmetry, the upward shift of the defect level is not as large as the CBM. This increases the energy separation of the defect level from the CBM, thus making the defect level deeper relative to the CBM edge. Similarly, for the acceptor states, because they contain some CBM *s* characters in their wave functions due to the reduced symmetry, the downward shift of the defect level is not as large as the VBM. This increases the energy separation of the defect level from the VBM, thus making the defect level deeper relative to the VBM edge.

It is interesting to see how the transition energy levels shift in an absolute energy scale. To check this, we have plotted in Fig. 5 the calculated acceptor transition energy levels of the group-III dopants in Si as a function of the QD size. Figure 6 presents the calculated donor transition energy levels of the group-V dopants in Si as a function of the QD size. In this plot, the band alignment is determined using our calculated band-gap change $\Delta E_g = \Delta E_c - \Delta E_v$ and the calculated value of Wang and Zunger,[23] that is, $\Delta E_v / \Delta E_c \sim 1.5$. It is important to mention that in most other semiconductors, the variation of ΔE_c is usually much larger than ΔE_v because the CBM state at Γ usually has a smaller effective mass than the VBM state. The trend is reversed in Si because its CBM is at a Δ point in the zinc-blende Brillouin zone, which has a larger effective mass than the VBM state at Γ. Using this band alignment, we find that for the group-III acceptors, the absolute transition energy level (i.e., with respect to vacuum) decreases as the QD size decreases due to downward shift of the VBM edge as the QD size decreases. On the other hand, for the group-V donors, the absolute transition energy level increases due to the upward shift of the CBM state. However, in either cases the variation within the QDs is relatively small with respect to the change of the band-edge states, indicating that for the small QDs studied here, the defect wave functions are already quite localized. Our results are consistent with previous observations.[14,15]

VI. SUMMARY

In summary, we have systematically calculated the defect formation energies and transition energy levels of group-III and group-V impurities doped in H passivated Si QDs as functions of the QD radius. We show that defect formation energy and transition energy level increase when the size of the QD decreases; thus, doping in small Si QDs becomes more difficult. For B impurity, we find that it is more stable near the surface than at the center of the Si QDs. On the contrary, P impurity tends to stay in the interior of the Si QDs. However, the stable position of the defects in the QDs may depend on the passivating agents. The general chemical trends and the variation as a function of the QD size are explained in terms of the atomic eigenvalues and quantum confinement effects.

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