

Influence of quantum dot shape on the formation energy of boron dopants in silicon

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ABSTRACT

A series of the formation energies E_f of boron dopants in Si quantum dots with different shapes, including tetrahedron (TH), tetrahedron-centered (TC), and octahedron (OT), are investigated by the first-principle calculation. The site of B dopants can be simply divided into vertex ("v"), edge ("e"), and facet ("f") on the surfaces of the Si quantum dots. It is found that the E_f value is strongly relying on quantum dot shape. In particular, when the size is given, one finds that TH shape has the lowest E_f values, while OT shape possesses the largest ones, and thus there is a sequence of $E_f(\text{TH}) < E_f(\text{TC}) < E_f(\text{OT})$. This can be well explained by the shape factor λ since the same sequence of $\lambda(\text{TH}) < \lambda(\text{TC}) < \lambda(\text{OT})$ exists. Interestingly, for each shape of TH, TC, and OT, λ is not a constant, behaving as the increasing trend when the size increases, while it behaves in decreasing trend for E_f . This means that the shape and the size have the opposite roles in E_f . Thus, considering the shape influence, one can say that the Si quantum dot with a smaller λ value is in favor of B dopants in them.

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I. INTRODUCTION

Si quantum dots have been an attractive subject of many experimental and theoretical studies in recent years.^{1–3} The higher surface/volume ratio makes Si quantum dots possess completely different physical properties from the bulk Si material.⁴ Except size, their shape is also one factor resulting in the change of the surface/volume ratio in Si quantum dots.^{5,6} With the ease of modifying the properties by tuning size and shape, the study on Si quantum dots has been greatly motivated because of their tremendous potential applications in photovoltaics,² optoelectronics,³ and bioimaging.^{7–9}

As reported, reducing the size will increase the energy gaps of Si quantum dots, and then their solar light harvesting is enhanced.¹⁰ At the same time, a clear dependence of the bandgap on Si quantum dots' shape has been widely reported if the size is given.⁶ Moreover, in the previous work,¹¹ it is mentioned that the highly curved surfaces of Si quantum dots would dramatically reduce their optical gaps and then further modulate excitonic lifetimes. Similar situations happen in the cases of impurity dopants in Si quantum dots.^{12,13}

As is known, boron (B) atom is the most widely used p-type dopant since it has high solubility in silicon and good ionization efficiency at room temperature. Many theoretical and experimental studies have shown that the formation ability of B dopants in Si quantum dots is influenced by a number of factors, including size,

shape, chemical environment,^{13–16} etc. For example, Xu *et al.*¹⁷ systematically calculated the defect formation energies E_f of group-III and group-V impurities in Si quantum dots, and a stronger size dependence on E_f was found. Similarly, it is reported that the larger the size implies the stronger formation ability of the impurities in Si materials.^{18,19} On the other hand, shape also plays an important role in E_f . As observed in Ref. 14, B dopants will cost more energy if Si quantum dots have more surface atoms in a given volume. If considering the difference in surface shape, the calculated formation energy is -70.85 eV for B dopants in $\text{Si}_{179}\text{H}_{148}$ quantum dot with spherical shape,²⁰ while it is 0.97 eV in $\text{Si}_{147}\text{H}_{100}$ with (113)-terminated shape.¹⁷ Despite the fact that the E_f values of B dopants are related with Si quantum dot shape, the qualitative or quantitative shape influence on E_f is still not completely clear.

Therefore, in this work, three shapes of Si quantum dot are picked up, tetrahedron (TH), tetrahedron-centered (TC), and octahedron (OT), to study the shape effect on the formation energy E_f of B dopants in them. By using the first-principle calculations, a series of E_f values are obtained for B atom separately doping at the vertex ("v"), edge ("e"), and facet ("f") sites on the surface of these Si quantum dots. Except size and site roles, shape also has an important role in E_f . Under certain size and site, we have $E_f(\text{TH}) < E_f(\text{TC}) < E_f(\text{OT})$; this sequence almost always exists and

can be validly applied to B dopants in these Si quantum dots. All this can be well explained if one introduces the shape factor λ , since λ has a similar sequence for these three shapes, i.e., $\lambda(\text{TH}) < \lambda(\text{TC}) < \lambda(\text{OT})$. It is also found that the role of shape in E_f is opposite to that of size.

II. COMPUTATIONAL DETAILS

All the calculations have been performed using the Cambridge Sequential Total Energy Package (CASTEP)²¹ within the generalized gradient approximation (GGA) with the Perdew–Wang exchange correlation functional (PW91). The core electrons were described using Vanderbilt ultrasoft pseudopotentials.²² The Monkhorst–Pack scheme k-points grid sampling was set at

$1 \times 1 \times 1$, and the tested plane wave kinetic energy cutoff of 450 eV was used. More than 15 Å of vacuum separates neighbor quantum dots in all the considered systems to prevent interactions between the periodic replicas. The optimized structures of Si_n quantum dots saturated by H atoms^{23,24} with TH, TC, and OT shapes are shown in Fig. 1, and the formation energies E_f of B atom doped in them can be deduced by the following expression:²⁵

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

where $E(\text{Si}_{n-1}\text{BH}_m)$ and $E(\text{Si}_n\text{H}_m)$ separately represent the total energy of the doped and undoped Si quantum dots. The subscripts

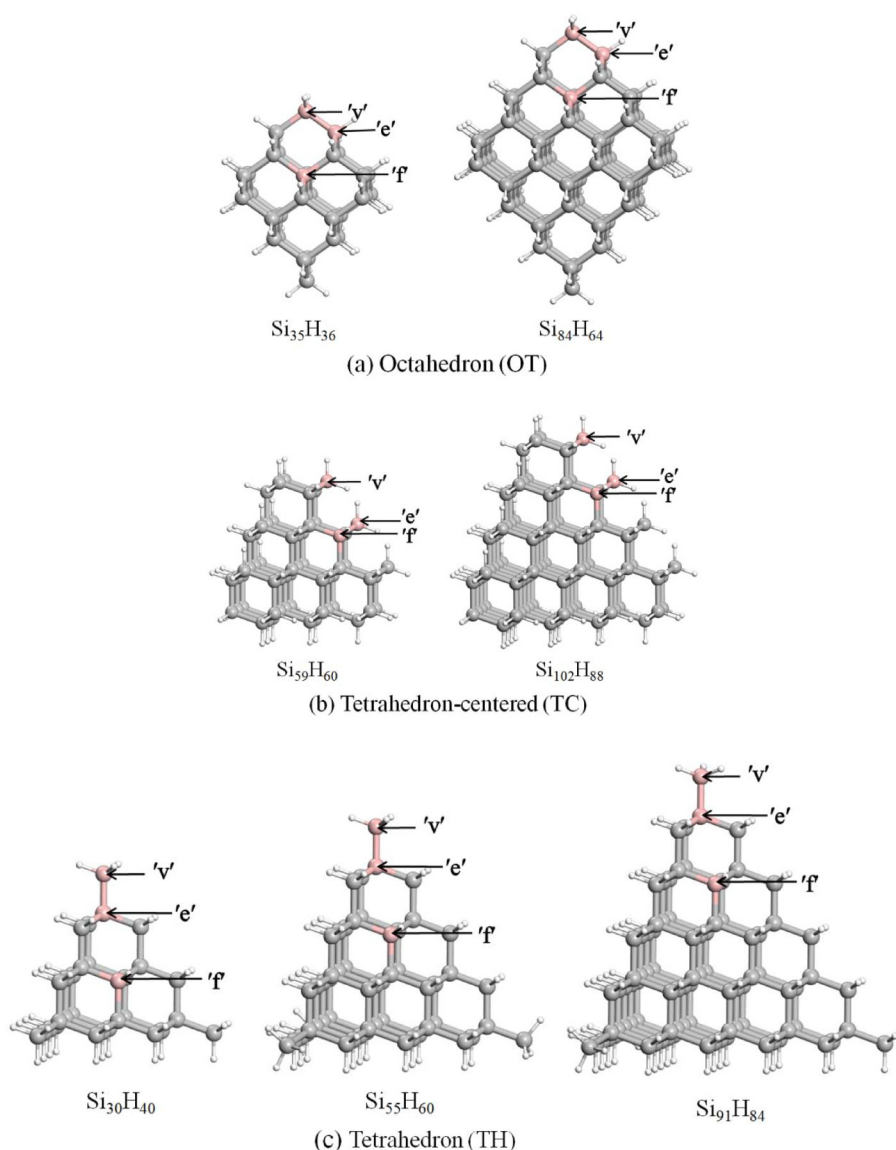


FIG. 1. The optimized structures of the Si quantum dots with the shape of (a) octahedron (OT), (b) tetrahedron-centered (TC), and (c) tetrahedron (TH). H, Si, and B atoms are denoted by white, gray, and pink balls, respectively. The symbols of “v”, “e,” and “f” show the B doping sites at the vertex, edge, and facet sites on the surfaces of Si quantum dots.

“n” and “m” mean the numbers of Si and H atoms, respectively. μ_{Si} and μ_{B} are the chemical potentials of Si and B atoms.^{12,15,26}

III. RESULT AND DISCUSSION

For these Si quantum dots, the formation energies E_f of B doping at different sites are summarized in Fig. 2. Obviously, a decreasing trend of E_f with size increasing is observed for Si quantum dots, respectively, with TH, TC, and OT shapes, which is consistent with the previous results.^{17–19} It should be noted, except the size effect on E_f , one can still find the obvious change of E_f with the shape. The Si quantum dots with TH shape almost always possess the lower E_f values, while those with OT shape have the largest ones. In particular, when the size of Si quantum dots is given, the shape effect is greatly obvious, and the sequence of $E_f(\text{TH}) < E_f(\text{TC}) < E_f(\text{OT})$ can be found. As expected, shape has become one of the important factors in determining the nanomaterials' properties, since the similar shape influences have been confirmed in many researchers, such as on the thermodynamic properties of nanomaterials.^{8,9} However, it is greatly necessary if the quantitative determination of the shape influence is resolved. Thus, based on shape consideration in the previous literature,^{8,9} shape factor λ is introduced in this work.

For nanomaterials or quantum dots, if their volume is given, their completely different properties arise from the different surface/volume ratio, which is directly determined by their shape. So, according to the surface atoms contribution and simultaneously taking a spherical shape as the reference, λ can be simply defined as the ratio of the surface/volume (δ') in a nonspherical shape to that (δ) in a spherical shape when they have an identical volume or n value. That is,

$$\lambda = \delta' / \delta. \quad (2)$$

If we let n_s be the surface atom number in a Si quantum dot, there is δ' (or δ) = n_s/n . Considering the Si crystal structure and the lattice packing density η , λ can be simplified as the following expression:⁸

$$\lambda = \frac{[n_s/n]}{6\text{times}\sqrt[3]{\eta/n}}, \quad (3)$$

where $\eta = 0.34$ is utilized, because all TH, TC, and OT shapes are the segments of a diamond cubic lattice structure.²⁷ From Eq. (3), it is clear that the shape influence is just because of the difference

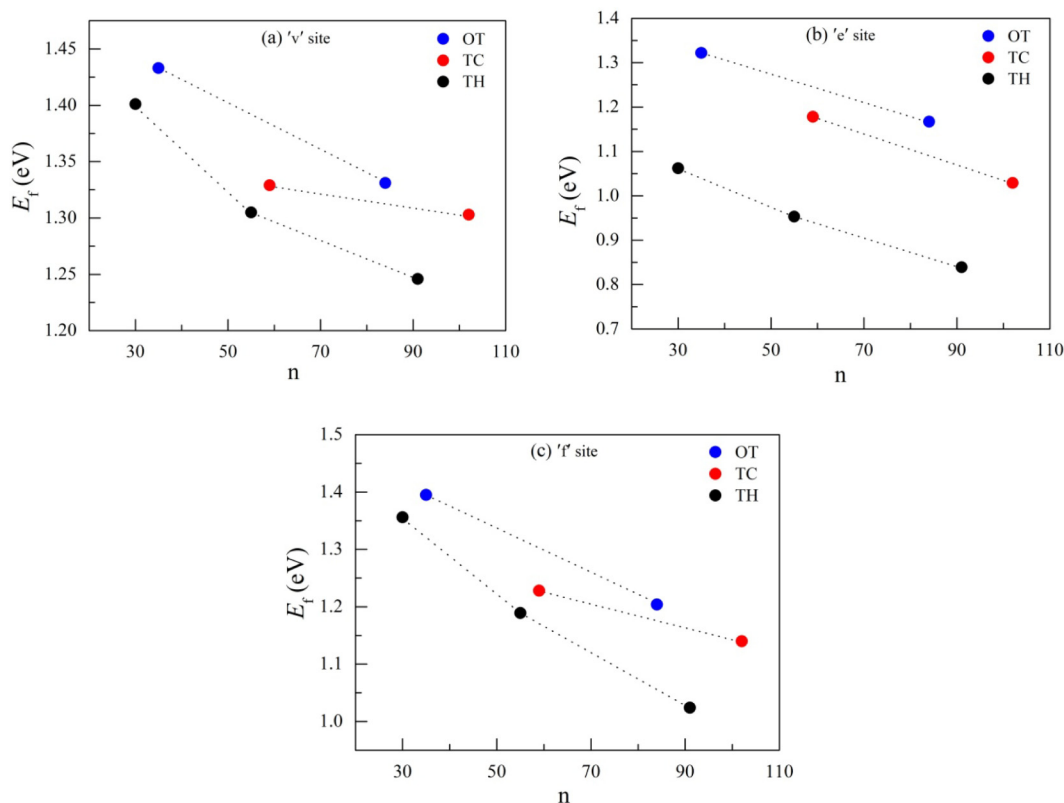


FIG. 2. The formation energy E_f of B doping at (a) vertex (“v”) site, (b) edge (“e”) site, and (c) facet (“f”) site in OT, TC, and TH structures.

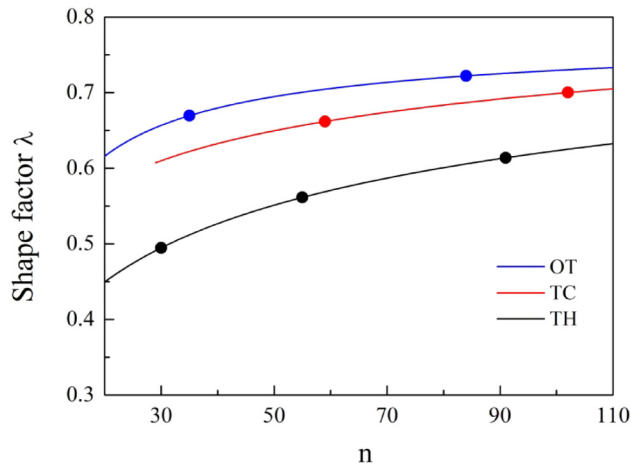


FIG. 3. The change in the trends of shape factor λ with size for OT, TC, and TH shapes.

in n_s . In addition, Eq. (3) also shows that in one shape, λ is still not a constant, closely relating with size.

In a regular geometrical shape of Si quantum dots, if we let “ q ” be the atom number on one edge, the value of

n and n_s can well be mathematically resolved, as seen in the following:

For TH shape, we have

$$n_s = 2q^2 - 4q + 4, \quad (4.1a)$$

$$n = q^3/3 + q^2/2 + q/6. \quad (4.1b)$$

For TC shape, we have

$$n_s = 2q^2 + 8q, \quad (4.2a)$$

$$n = q^3/3 + 21q^2/6 + 37q/6. \quad (4.2b)$$

For OT shape, we have

$$n_s = q^2 + 2q - 5, \quad (4.3a)$$

$$n = q^3/6 + q^2/2 + q/3. \quad (4.3b)$$

Based on Eqs. (3) and (4), Fig. 3 displays the curves of λ for Si quantum dots with TH, TC, and OT shapes. It is evident that λ is not only relying on the size, but also on the shape. For any shape, there is always an increasing trend of λ with an increase in size n .

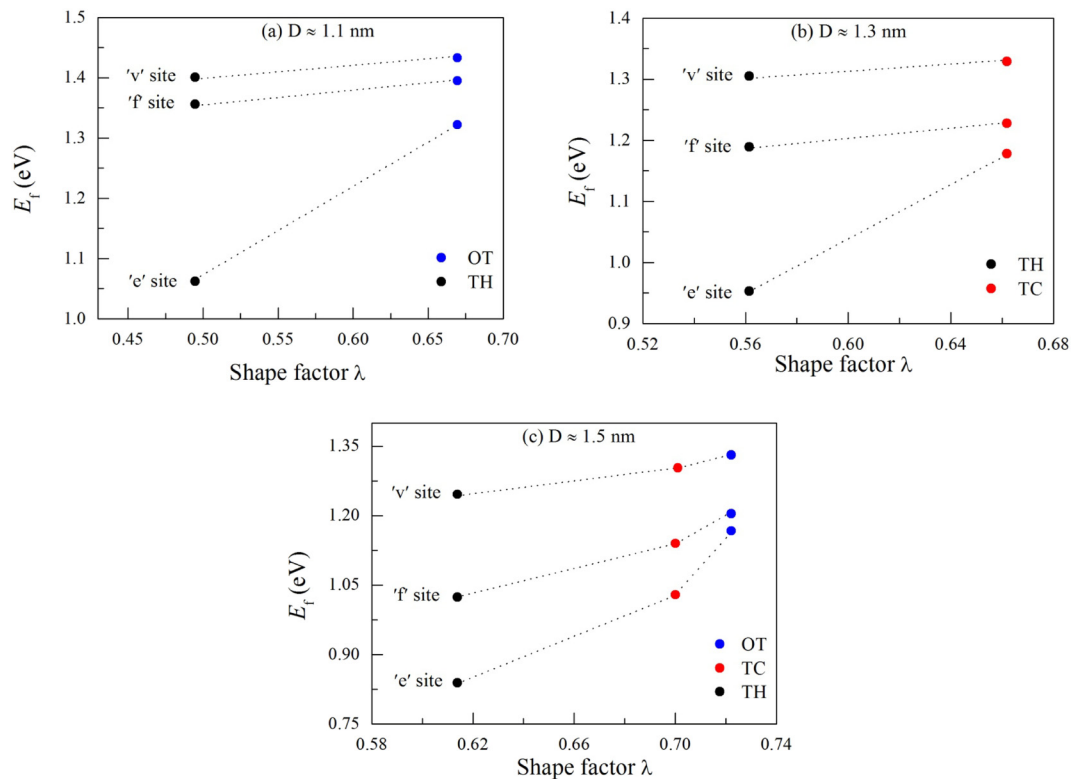


FIG. 4. The change of E_f with the shape factor λ at (a) $D \approx 1.1$ nm, (b) $D \approx 1.3$ nm, and (c) $D \approx 1.5$ nm.

Moreover, it should be mentioned that when n is certain, the sequence of $\lambda(\text{TH}) < \lambda(\text{TC}) < \lambda(\text{OT})$ exists, and even this can be expanded in a full size range. Interestingly, this sequence in λ is consistent with the sequence of E_f [$E_f(\text{TH}) < E_f(\text{TC}) < E_f(\text{OT})$], as displayed in Fig. 2. So, to some extent, one can say that the increase in λ will result in the increase in E_f .

In fact, to further make clear the relationship between shape and E_f , the size or the n value in Si quantum dots should be given. So, the diameter D of a spherical dot is used, where D is defined as the diameter of a spherical dot which has the same atom number with Si quantum dots with nonspherical shape. The determination of the D value can be seen in Ref. 8, and one can read

$$D = h \times \sqrt[3]{n/\eta}, \quad (5)$$

where h ($= 0.235$ nm) represents the diameter of Si atom. In such a way, the shape effect on E_f will become more obvious. As shown in Fig. 4, the increasing trend of E_f with the increase in λ value is further reflected. That is to say, the quantitative determination for shape factor presents a valid way to discriminate B doping ability in Si quantum dots with different shapes. It should be noted that to clarify the shape influence, the size of the Si quantum dot and the

doping site of B atom should be fixed, since E_f is also related with them.

Figure 4 shows the site influence on E_f , and one can find that “e” is usually the preferred site for B doping, followed by “f” and “v” sites for these Si quantum dots with TH, TC, and OT shapes. Evidently, there is a little complicity if one wants to make the B doping ability in Si quantum dots clear. This is because size, site, and shape are the three basic parameters in determining their E_f values. So, when the size consideration for E_f is required, the doping site and the shape of the Si quantum dot should be known, while the site influence will become clear until the size and shape parameters are given. Similarly, the shape consideration in this work is also under the prediction that the size of Si quantum dots and B doping site are fixed. This is similar to the size and shape contributions in thermodynamic properties of nanomaterials.^{8,9} Anyway, shape factor λ becomes an effective method to describe the shape difference among the Si quantum dots.

Finally, from the point of energy, the energy state of a Si quantum dot is directly related with its physical properties. So, to further expand the application of E_f in Si quantum dots, Fig. 5 is made, where the relationship between E_f and bandgap E_g is presented. Clearly, the increase of E_f is along with the increase in E_g , which means that the B-doped Si quantum dot with larger E_f value will have a larger bandgap. So, based on the observances on the size-, shape-, and site-related E_f values, the bandgap of B-doped Si quantum dots may be at some extent predicted, which will be helpful in providing the guidance for their application.

IV. CONCLUSION

The formation energy E_f of B dopants in Si quantum dots with TH, TC, and OT shapes is well studied by the first-principle calculation. The calculation results show that the consideration of size, shape, and site is necessary to clarify the B doping ability in Si quantum dots. For a shape effect, the sequence of $E_f(\text{TH}) < E_f(\text{TC}) < E_f(\text{OT})$ is clearly observed, which can be well attributed to the difference in shape factor λ . A similar sequence of $\lambda(\text{TH}) < \lambda(\text{TC}) < \lambda(\text{OT})$ is obtained, implying that the increase in λ will result in the increase in E_f . That is to say, the larger surface/volume ratio will be in favor of B dopants in Si quantum dots. In addition, a clear relationship between E_f and the bandgap of Si quantum dots is found, well expanding the application of E_f into the predictions on the physical properties.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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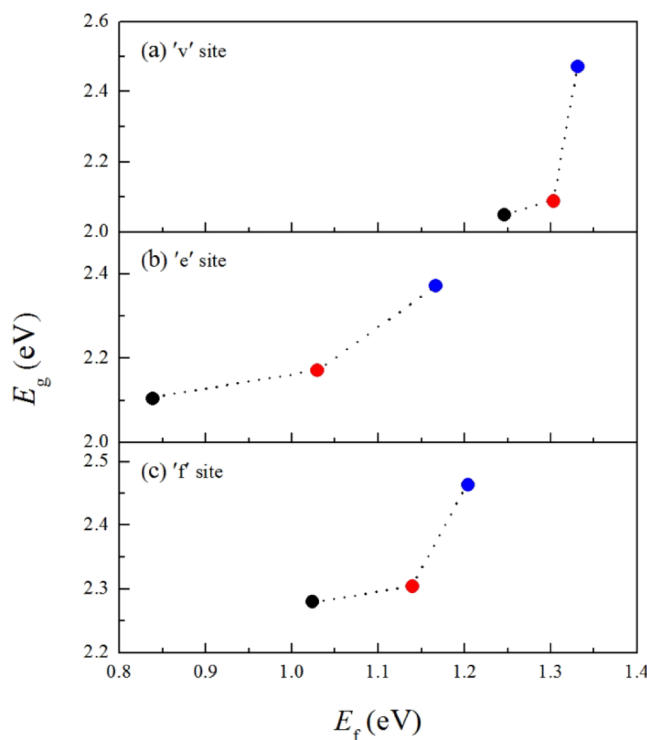


FIG. 5. The relation between E_f and E_g for the B-doped Si quantum dots when B is separately doped at (a) “v” site, (b) “e” site, and (c) “f” site. The black symbols represent the TH shape, the red symbols represent the TC shape, and the blue ones represent the OT shape.

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