

Stability of the DX^- Center in GaAs Quantum Dots

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Using a first-principles band structure method, we study how the size of quantum dots affects the stability and transition energy levels of defects in GaAs. We show that, although a negatively charged DX^- center is unstable in bulk GaAs:Si with respect to the tetrahedral coordinated Si_{Ga}^- , it becomes stable when the dot size is small enough. The critical size of the dot is about 14.5 nm in diameter. The reason for the stabilization is the strong quantum-confinement effect, which increases the formation energy of Si_{Ga}^- more than that of the DX^- defect center. Our studies show that defect properties in quantum dots could be significantly different from those in bulk semiconductors.

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Semiconductor nanocrystals such as quantum dots (QDs) [1] are of great current interest for technological applications, because the physical properties of QDs (such as band gap and optical transitions) can be tailored continuously by size and/or shape, thus opening up a great potential for novel device applications. On the other hand, the application of semiconductors as novel electronic devices depends critically on their doping properties. Most semiconductor compounds will not be very useful if not enough charge carriers are generated by the dopants at normal working temperature [2]. Although defect properties have been extensively studied in the past for bulk semiconductors and various approaches have been proposed to overcome the doping limit in semiconductors [3], very few studies have been carried out to understand how the formation of QDs affect the defect properties in semiconductors [4]. For example, it is not clear how the size of QDs affects the defect formation energies and ionization energy levels, as well as the relative stability between different defects.

The DX -like defect center, which converts a shallow hydrogenic donor into a deep level acceptor [5–8], is one of the major “killer” defects that limits n -type doping in II-VI and III-V semiconductors [9,10]. The DX centers in bulk semiconductors have been intensively studied for many years [5–15]. The original single-bond-breaking model, proposed by Chadi and Chang [11] for Si-doped GaAs, suggests that the DX center forms by displacing the substitutional Si defect along the $\langle 111 \rangle$ direction, breaking one bond and changing the local symmetry from T_d to C_{3v} [Figs. 1(a) and 1(b)]. Accompanied by the displacement, the t_{2c} state in the conduction band splits into an a_1 and a doubly degenerate e state. The resulting $a_1(t_{2c})$ state couples with the original $a_1(a_{1c})$ state, pushing one of them down [Fig. 1(c)]. If the a_1 state is occupied (preferentially by two electrons, such as in Si_{Ga}^-), such an atomic-displacement-induced level repulsion can lead to electronic energy

gain [10], although breaking the bond in the $\langle 111 \rangle$ direction also costs energy. When the DX center becomes stable, it converts a shallow donor (e.g., Si_{Ga}^+) into a deep acceptor [e.g., $DX(Si_{Ga}^-)$], thus limiting the doping process.

In this Letter, we study, as an example, the formation of DX centers in Si-doped GaAs as a function of QDs size. In bulk GaAs, if Si replaces a Ga in GaAs [Fig. 1(a)], it will produce a shallow donor level at about 5 meV below the conduction band minimum (CBM). In this case, the Si-related DX center is found to be unstable [11]. However, it has been shown that under a hydrostatic pressure greater than ~ 20 kbar [7,8], or alloying with AlAs to form $Al_xGa_{1-x}As$ alloys with $x > 0.22$ [5,6], $DX(Si_{Ga}^-)$ can be stabilized. Here, we show that reduced dimensionality and size can also cause stabilization of DX centers in GaAs:Si QDs. This is because the quantum confinement increases the CBM energy and lowers the valence band maximum (VBM) energy, thus increasing the band gap (Fig. 2). For

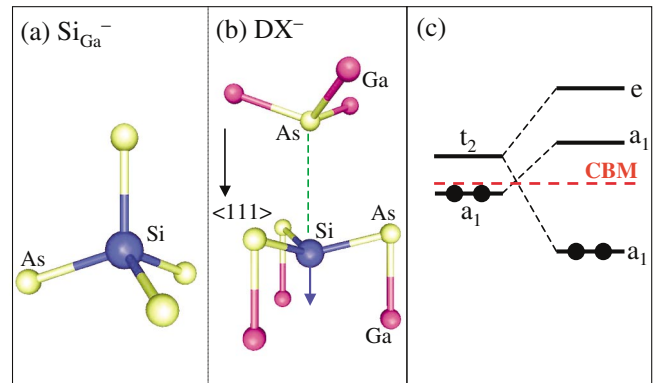


FIG. 1 (color online). A schematic plot of (a) the tetrahedral coordinated Si_{Ga}^- ; (b) DX^- with Si displaced along the $\langle 111 \rangle$ direction. Panel (c) shows schematically how the DX^- center can be stabilized by lowering the electronic energy and converting a shallow donor to a negatively charged deep acceptor.

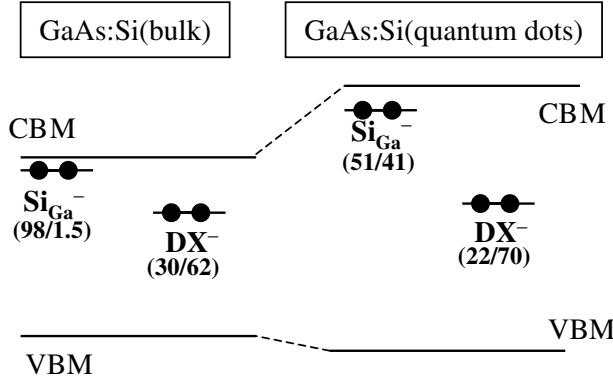


FIG. 2. Schematic illustration of the variation of energy levels of Si_{Ga}^- and DX^- in bulk GaAs and GaAs QDs. The numbers in parentheses indicate the projected s/p characters of the defect states for bulk and QDs with $d = 2.69$ nm.

the negative-charged Si_{Ga}^- at the T_d site, the shallow defect level has mostly CBM character; thus the energy level of Si_{Ga}^- follows closely with CBM (Fig. 2). But for the DX^- center, the defect level has a significant amount of non-CBM character, so the DX^- level does not follow closely to the CBM (Fig. 2). Therefore, in QDs, when the CBM increases, the formation energy of Si_{Ga}^- increases faster than that of DX^- , thus stabilizing the DX^- center. Our calculations for the formation of DX^- centers in GaAs:Si QDs, therefore, demonstrate that defect physics in small size QDs could be very different from that in bulk semiconductors.

The calculations are performed within the local density approximation (LDA) [16] as implemented in the VASP code [17]. Large cell calculations have also been tested using the charge patching method [18]. We use the Vanderbilt ultrasoft pseudopotential [19]. The wave functions are expanded in a plane-wave basis set with the cutoff energy equal to 150 eV. The calculated lattice constant of GaAs and Si are 5.588 and 5.386 Å, respectively, in good agreement with experimental values [20] of 5.653 and 5.412 Å. The calculated band gap of GaAs at the Γ point is 0.651 eV, which is smaller than the experimental value [20] of 1.52 eV due to the LDA band gap error.

The QDs are constructed by including all atoms within a given radius. The surface atoms of QDs are fixed at their ideal zinc-blende position and are passivated by pseudo-H atoms (1.25 charge H to passivate the surface Ga-atom dangling bonds, and 0.75 charge H to passivate the surface As-atom dangling bond) [21]. In this study, we consider two experimentally accessible dot sizes with diameters of 1.55 and 2.69 nm, including 87 and 453 atoms, respectively. The QDs are calculated using the supercell approach [21], where the QDs are put at the lattice site of a large simple cubic cell and separated by vacuum regions to avoid dot-dot interaction. Periodic boundary conditions are applied. The supercell size is $3a \times 3a \times 3a$ for the 1.55 nm QD and $5a \times 5a \times 5a$ for the 2.69 nm QD, where a is the lattice constant of GaAs.

To calculate the defect formation energy and defect transition energy levels, we put the defect at the center of the QDs. All the internal atoms are relaxed by minimizing the quantum mechanical force and total energy until the changes in the total energy are less than 0.1 meV/atom. Our total-energy calculations for the passivated QDs indeed find that the defects are more stable at the center of the QDs. For charged defects, a uniform charge background is introduced to keep the charge neutrality of the supercell. For the bulk calculation, we used a 64-atom cell. To partially correct the LDA band gap error [3], we performed the calculation at the special k points where the band gap is 1.38 eV, close to the experimental value [20]. We first calculate the total energy $E(\alpha, q)$ for the system containing the relaxed defect α in charge state q , as well as the total energy $E(\text{host})$ of the host for the same supercell in the absence of the defect. We also calculate the total energies $E(i)$ of the involved elemental solids at their respective stable phases. From these quantities, we can deduce the defect formation energy $\Delta H_f(\alpha, q)$ as a function of the electron Fermi energy E_F , as well as the atomic chemical potentials μ_i :

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + \sum n_i \mu_i + q E_F, \quad (1)$$

where $\Delta E(\alpha, q) = E(\alpha, q) - E(\text{host}) + \sum n_i E(i) + q \varepsilon_{\text{VBM}}(\text{host})$. Here, E_F is referenced to the VBM of the host, μ_i for the element i is referenced to the elemental solid with energy $E(i)$, n_i is the number of elements, and q is the number of electrons transferred from the supercell to the reservoirs in forming the defect cell [3]. The defect transition energy level then can be determined using

$$\varepsilon_\alpha(q/q') = [\Delta E(\alpha, q) - \Delta E(\alpha, q')]/(q - q'). \quad (2)$$

A more detailed description of the QD and defect calculations can be found in Refs. [3,21].

Figure 3(a) shows the formation energy of neutral Si_{Ga}^0 in GaAs QDs as a function of the diameter of the dot. The diameter $d = \infty$ corresponds to the bulk system. The errors in the formation energy due to the underestimated LDA band gap for this shallow donor state have been corrected by adding the energy difference between the experimental and calculated band gaps. As the size of the QDs decreases, the formation energy of Si_{Ga}^0 increases from 1.55 eV for bulk GaAs:Si to 2.99 eV for QD with $d = 1.55$ nm. This increase is because Si_{Ga}^0 creates a singly occupied level near the CBM. This level has a strong CBM s character and moves up in energy with the CBM as the QDs size decreases, thus increasing the formation energy. However, because this defect level is not a pure CBM state (Fig. 2), as the CBM moves up in energy with the decreasing QDs size, the energy difference between the defect level and the CBM, thus the $(0/+)$ transition energy level from the CBM, also increases. The calculated results are shown in Fig. 3(b). We find that the calculated $\varepsilon(0/+)$ transition energy of Si_{Ga}^0 is very shallow at 6 meV below CBM in the

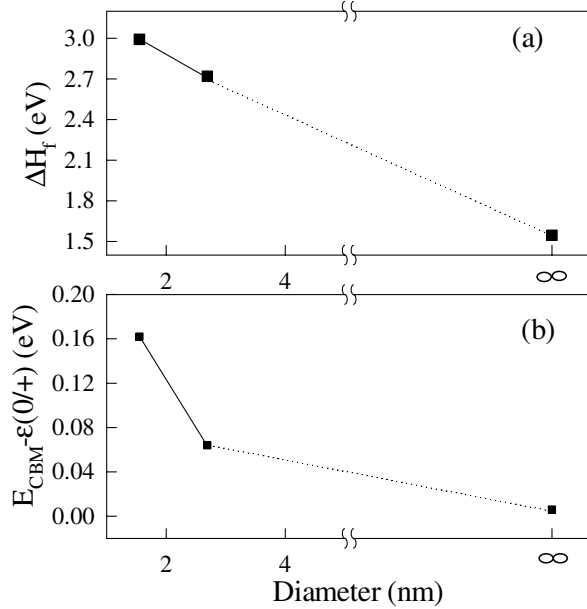


FIG. 3. (a) The formation energy of neutral Si_{Ga}^0 in GaAs:Si at $\mu_i = 0$ and (b) the transition energy $\epsilon(0/+)$ (referenced to CBM) of Si_{Ga} in GaAs:Si as a function of the QDs diameter.

bulk system, in good agreement with experimental results [20]. It increases to 162 meV for the smallest QD studied in this work. These results indicate that n -type doping using Si as dopant will be much more difficult in small QDs than in bulk GaAs.

The LDA-calculated Ga-As bond length in pure GaAs is $d_0 = 2.42$ Å. For bulk GaAs:Si, the Si-As bond lengths of Si_{Ga}^+ , Si_{Ga}^0 , and Si_{Ga}^- are 2.375, 2.377, and 2.378 Å, respectively, slightly smaller than d_0 . The small increase of the bond length as q decreases from +1, 0, to -1 is consistent with the fact that the As atom in GaAs is negatively charged; therefore, when Si_{Ga} becomes more negatively charged, Coulomb repulsion will push As away, increasing the Si-As bond length. However, because the Si_{Ga} level is very shallow, that is, the defect charge is delocalized [Fig. 4(a)], the variation of the bond length as a function of q is rather small. However, in small QDs with diameter $d = 1.55$ nm, the Si-As bond length increases significantly for Si_{Ga}^+ , Si_{Ga}^0 , and Si_{Ga}^- , changing from 2.387, to 2.438, to 2.489 Å, respectively. This is consistent with the fact that the Si_{Ga} level is deep and more localized around Si in the QDs [Fig. 4(c)]; thus changing the charge state at a Si site will have a large effect on the Coulomb interaction and lead to a large variation of the Si-As bond lengths.

Finally, we study the relative stability of the DX center in GaAs:Si QDs. The DX formation energy is defined as the energy difference [22]

$$\Delta E(DX) = E(DX^-) - E(\text{Si}_{\text{Ga}}^-), \quad (3)$$

where $E(DX^-)$ is the total energy of the negatively charged DX^- center and $E(\text{Si}_{\text{Ga}}^-)$ is the total energy of the corresponding tetrahedral coordinated defect Si_{Ga} at the same

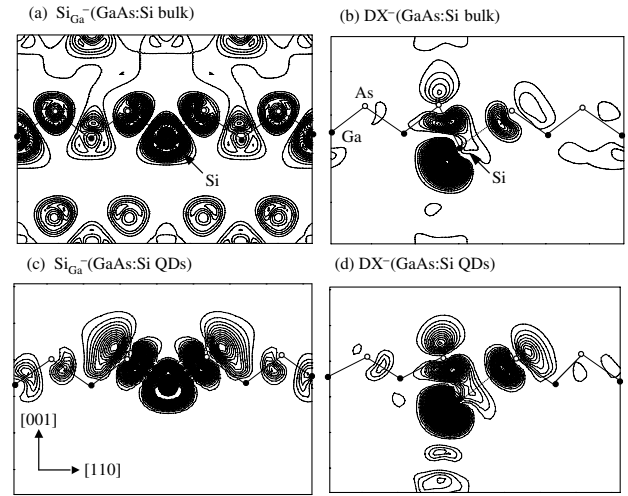


FIG. 4. Contour plot of the charge density distribution around Si defects for (a) Si_{Ga}^- and (b) DX^- of bulk GaAs:Si and (c) Si_{Ga}^- and (d) DX^- of GaAs:Si QDs (diameter $d = 2.67$ nm).

charge state. A negative $\Delta E(DX)$ will indicate that the DX center is more stable than the Si sitting at the substitutional Ga site. The calculated results are shown in Fig. 5. In bulk GaAs, the Si-doped DX formation energy is positive, indicating that the formation of a DX center is not favored in bulk GaAs:Si. However, as the size of the QDs decreases and the corresponding band gap E_g increases, the DX formation energy becomes less positive and changes sign when the band gap is close to $E_g = 1.78$ eV, which is about 0.26 eV larger than the experimental band gap. We have previously shown [21] that the band gap increases of GaAs QDs due to quantum confinement can be expressed as $\Delta E_g = 3.88/d^{1.01}$, where d is the diameter of the QDs. Using this expression, we estimate that the Si DX center in GaAs will become stable when the diameter of the QD is less than 14.5 nm.

The origin of the enhanced stability of the DX center due to quantum confinement can be understood as follows: The

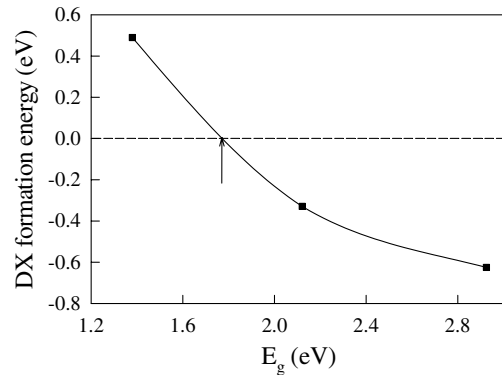


FIG. 5. DX formation energy as a function of the calculated band gap of GaAs QDs. The arrow indicates the band gap $E_g = 1.78$ eV, at which the DX^- is stabilized. The corresponding QD diameter is about 14.5 nm.

quantum confinement increases the CBM energy. For the negative-charged Si_{Ga}^- at the T_d site [Fig. 1(a)], the shallow defect level has mostly CBM s wave-function character. Thus, the energy level of Si_{Ga}^- follows closely with the CBM (Fig. 2). But for the DX center, the Si impurity undergoes a large Jahn-Teller distortion along the $\langle 111 \rangle$ direction [Fig. 1(b)]. Consequently, the level repulsion between the $a_1(a_{1c})$ with $a_1(t_{2c})$ states mixes a significant amount of atomic p orbital into the wave function, so the DX^- level does not follow closely to the CBM (Fig. 2). Therefore, in QDs, when the band gap increases, the energy difference between the occupied DX^- and Si_{Ga}^- levels also increases, thus stabilizing the DX center.

This quantum-confinement effect is similar to the effect induced by the hydrostatic pressure or alloying with AlAs in Si-doped GaAs. Under hydrostatic pressure, the DX center is stabilized when the pressure is greater than 20 to 30 kbar [7,8], which corresponds to an increase of the band gap by about 0.25 eV [20]. In forming the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy, DX is stabilized when $x > 0.22$ [5,6], which corresponds to an increase of the band gap by about 0.3 eV [20]. These results are consistent with our finding that when quantum confinement increases the band gap of GaAs QDs by about 0.26 eV, the DX^- center becomes more stable than the tetrahedral Si_{Ga}^- defect in GaAs. It also suggests that independent of the shape or surface treatment of the QDs, when the band gap of the QDs increases due to the quantum confinement, the DX^- center will become more stable.

In summary, using first-principles total-energy calculations, we have shown that defect properties in QDs could be very different from those in bulk semiconductors. We predict that n -type doping in GaAs QDs will be much more difficult in small-sized QDs than in bulk and that a self-compensating DX center will become stable when the dot size is reduced to less than 14.5 nm in diameter.

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