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n-type doping via avoiding the stabilization of *DX* centers in InP quantum dots

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We demonstrate that it is preferable to dope III-V semiconductor nanocrystals by *n*-type anion substitution as opposed to cation substitution. Specifically, we show the dopability of zinc-blende nanocrystals is more efficient when the dopants are placed at the anion site as quantified by formation energies and the stabilization of *DX*-like defect centers. Our results are based on first-principles calculations of InP quantum dots by using a real-space implementation of density-functional theory and pseudopotentials.

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The search for new materials that would serve as basis for highly integrated devices in semiconductor industry within the deep nanometer regime is of tremendous current interest. Among these materials, semiconductor nanocrystals such as quantum dots (QDs) are especially important.[1] Besides their reduced dimension, QDs offer the possibility to control the properties of their macroscopic counterparts (such as the band gap) by controlling their physical size. Here we show that an analysis based on quantum confinement can be used to determine how to efficiently dope nanostructures, i.e., we demonstrate that *n*-type doping of zinc-blende nanostructures is more efficient when the dopants are placed at anion sites.

Electronic and optoelectronic functional devices require the semiconductors to be functionalized via *p*-type and *n*-type doping. Among the most relevant factors that impede the efficient dopability of semiconductors are the low solubility of the impurity atom and the formation of defects that would inhibit the desired characteristics of the impurity states. The solubility of the dopant can be evaluated from its formation energy, which is a measure of the energy cost derived from the introduction of the dopant into the host material. Here we will restrict ourselves to *n*-type materials. The most relevant defects present in II-VI and III-V semiconductors are *DX* centers,[2] which create a donor state that was initially shallow to be located deep within the host band gap.

One expects the dopability in semiconductor QDs to be reduced when compared to the bulk materials owing to restricted solubility and energetically unfavorable formation energies. Specifically, the formation energy of substitutional dopants in *p*-type and *n*-type Si-QDs was found to increase, i.e., be less favorable, as the size of the QDs decreases.[3] Likewise, the situation was found to be more unfavorable in *n*-type GaAs-QDs doped at the cation site, since the increase in the formation energy of the dopant was also found to be accompanied by the stabilization of *DX* defect centers.[4] However, III-V semiconductor QDs can be doped at *both* cation and anion sites. The question we wish to explore is whether such unfavorable doping trends will be true for both sites, i.e., will the formation energies become less favorable for doping and will defects be stabilized by a reduction in the physical size of the system for both the cation and anion sites?

Here we carry out a detailed study of the formation energy and possible stabilization of *DX* centers in *n*-type InP-QDs showing that III-V semiconductor QDs with zinc-blende structure should not be doped by cation substitution but rather by anion substitution. We find that the formation energies increase with decreasing size of the nanocrystal for a dopant at both cation and anion sites; however, the formation of *DX* centers is favored when the dopant is placed at the cation site compared to the anion site.

Our study is based on density-functional theory as implemented in the PARSEC code.[5] In this implementation, the Kohn-Sham equations are solved self-consistently on a three-dimensional real-space grid. Only one parameter, the grid spacing, is necessary to control numerical convergence. The core electrons are represented by norm-conserving pseudopotentials.[6] The local-density approximation is used for the exchange and correlation potential.[7] We have successfully employed this computational approach in the study of different *p*-type doped InP materials, including the bulk material,[8] nanowires,[9] and QDs.[10]

Spherical InP-QDs with diameters of 1.50, 1.82, and 2.36 nm were constructed from the zinc-blende structure of the bulk (these systems contain 87, 147, and 293 atoms of crystalline core, respectively). In and P dangling bonds at the surface were passivated using fictitious, hydrogenlike capping atoms with fractional charge.[11] The nanocrystals were chosen to be centered on both In and P atoms, which are the atoms that were replaced by the external impurity. As dopants, we used a Si atom that substitutionally replaces the cation ($\mathrm{Si_{In}}$), and a Se atom that substitutionally replaces the anion ($\mathrm{Se_P}$). All the atoms in the QDs were allowed to relax except those atoms at the surface. We introduced this constraint in order to mimic the effects of the coating layer that is normally used to passivate chemically semiconductor nanomaterials such as nanowires or QDs.

The replacement of a In (P) atom by a Si (Se) impurity introduces in the host nanocrystal a singly degenerate impurity state with a_1 symmetry and dominant s character. The impurity state is located at the dopant as shown in Fig. 1 and the T_d crystal symmetry in the vicinity of the impurity is preserved. We have computed the binding energy of the donor states in the QDs as the difference between the ionization

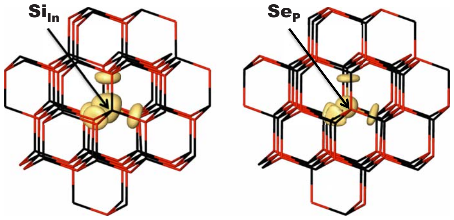

FIG. 1. (Color online). Charge density associated to the donor state introduced in the InP nanocrystal with diameter 1.50 nm by $\mathrm{Si}_{\mathrm{In}}$ (left panel) and Se_{P} (right panel) *n*-type doping. Black and red symbols stand for In and P atoms, respectively. Charge density is plotted at 30% of its maximum value.

energy and electron affinity of the doped and undoped nanocrystals, respectively. We extrapolated our calculations to the bulk limit by fitting to a power law that takes into account the binding energy being driven by an almost unscreened electron-hole Coulomb interaction, as it was done for *n*-type Si-QDs.[3] Since bulk InP has a large exciton Bohr radius, we have included nanocrystals in our calculations that contain thousand atoms of crystalline core, as we did when extrapolating the binding energy in *p*-type InP-QDs.[10] Our extrapolated binding energy vanishes in the bulk limit to within a value of 0.1 eV, which is in good agreement with the shallow character of donor states in the bulk as reported by experiment.[12]

The calculation of impurity formation energies requires chemical potentials of the elements that are exchanged in the nanocrystals.[4] These potentials refer to the energy of the particle reservoirs from which the atoms are taken and depend on the working environment. Since we are interested on the effects that quantum confinement has on the properties of interest, we can avoid the dependence on the chemical potentials by calculating the formation energies relative to the bulk by using the expression

$$\Delta E_f = [E_{T,\mathrm{QD}}(X_Y) - E_{T,\mathrm{QD}}(\text{undoped})] - [E_{T,\mathrm{bulk}}(X_Y) - E_{T,\mathrm{bulk}}(\text{undoped})], \qquad (1)$$

where $E_{T,\mathrm{QD}}$ and $E_{T,\mathrm{bulk}}$ represent the total energies of the nanocrystal and bulk systems, respectively, and $X_Y = \{\mathrm{Si}_{\mathrm{In}}, \mathrm{Se}_{\mathrm{P}}\}$. As we can see in Fig. 2, the formation energies increase monotonically with decreasing diameter of the nanocrystals as result of quantum confinement. This similar behavior of the formation energies can be explained from simple electronic structure arguments. Since both the $\mathrm{Si}_{\mathrm{In}}$ and Se_{P} impurity levels have dominant conduction-band minimum (CBM) *s* character (see Fig. 1), they will react similarly to confinement than this latter state, i.e., the levels move up in energy with decreasing diameter of the nanocrystal or increasing quantum confinement. And since both impurity levels are occupied by an electron, they will both contribute to the total energy of the QDs, thus increasing the formation energies of the dopants through an increase in the value of the first term in the right-hand side of Eq. (1) (the total energies of the doped QDs). Our results predict a lower impurity concentration in *n*-type InP-QDs when compared to the bulk because of energetic arguments and that this is independent on whether the dopants are placed at cation or anion sites. An increase in the formation energies of impurities in different nanocrystals was also found,[3,4,13] thus indicating that this could be an intrinsic property of these nanomaterials as noted in previous work.[13]

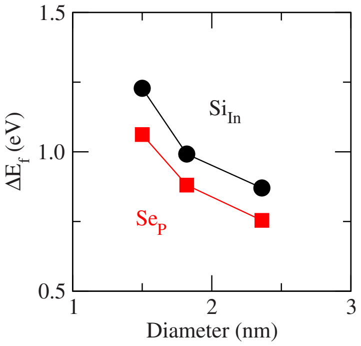

FIG. 2. (Color online). Relative formation energies of $\mathrm{Si}_{\mathrm{In}}$ (circles) and Se_{P} (squares) impurities introduced in InP-QDs as obtained from our first-principles approach.

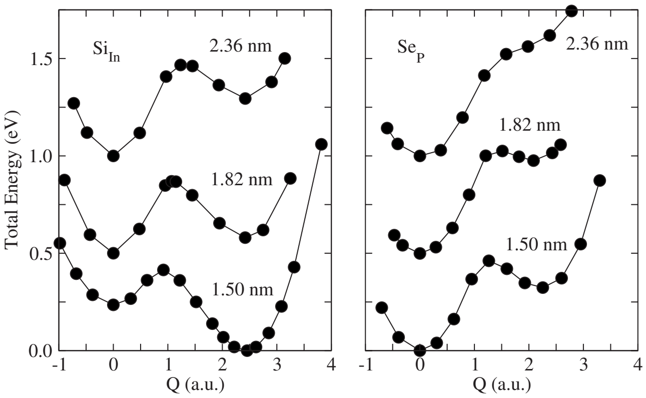

FIG. 3. Configuration coordinate diagrams of negatively charged $\mathrm{Si}_{\mathrm{In}}$ (left panel) and Se_{P} (right panel) doped InP-QDs.

In contrast to the behavior of the formation energy, we found important differences in the $\mathrm{Si}_{\mathrm{In}}$ and Se_{P} doped nanocrystals relative to the formation of *DX* centers. These centers correspond to negatively charged defects in which either the donor atom itself or one of its neighbors undergoes a bond-rupturing displacement along a crystal direction.[2] Defining as configuration coordinate Q the displacement of the dislocated atom respect to its ideal or undistorted position allow us to keep track of the energetics associated to this process.

In the left panel of Fig. 3 we represent the configuration diagrams obtained for the $\mathrm{Si}_{\mathrm{In}}$ doped InP-QDs. We found two local minimum configurations in the total energies of the negatively charged QDs. In one of these minima ($Q=0$), the extra electron occupies the impurity donor state (left panel of Fig. 1), and the T_d crystal symmetry is preserved. In the other local minimum configuration ($Q \sim 2.4$ a.u.), the Si atom breaks one of its bonds and undergoes a displacement along the $\langle 111 \rangle$ direction, adopting an interstitial site, which corresponds to the formation of the *DX* center (left panel of Fig. 4). In this latter configuration the crystal symmetry is lowered from T_d to C_{3v}. The transformation from the $\mathrm{Si}_{\mathrm{In}}^-$ con-

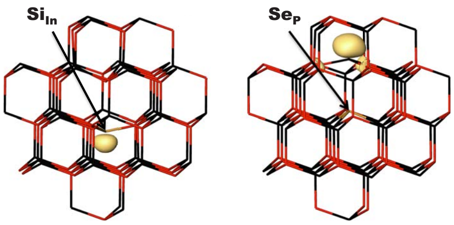

FIG. 4. (Color online). *DX* centers corresponding to the Si_{In} (left panel) and Se_P (right panel) doped InP nanocrystal with diameter 1.50 nm. The charge density associated to the eigenstate holding the donor-electron pair is also shown. Black and red symbols stand for In and P atoms, respectively. Charge density is plotted at 30% of its maximum value.

figuration to the *DX* configuration can be understood as driven by a Coulombic force. In the T_d configuration, the negatively charged Si impurity atom is bonded to four anion P atoms so it experiences a repulsive Coulombic force. This electrostatic force "pushes" the impurity atom into an interstitial region that surrounds it after passing through the energy barrier that is derived from the breaking of one of the Si-P bonds. Since the Coulombic interaction is stronger for the smaller QDs (the electronic wave functions are more localized in space), the energy barrier will increase with the size of the nanocrystal (the energy barriers for the QDs with diameters 1.50 nm, 1.82 nm, and 2.36 nm are 0.18 eV, 0.37 eV, and 0.47 eV, respectively).

The transformation from the Si_{In}^- configuration to the *DX* center introduces important changes in the electronic structure of the doped QDs and, in particular, in the energy level of the impurity donor state (see the left panel of Fig. 5). The reduction in the ionic symmetry in the nanocrystal is accompanied by the splitting of triply degenerate states having t_2 symmetry into singly (a_1 symmetry) and doubly (e symmetry) degenerate states. One of these triply degenerate states (t_{2c}; see the figure) gives a singly degenerate state $[a_1(t_{2c})]$ that strongly couples with the impurity donor state during the nanocrystal deformation. As result of this interaction, the impurity donor state acquires dominant p character and significantly lowers its position within the energy gap (it becomes a deep state). The electronic energy gain derived from this interaction has been attributed as the cause of stabilization of *DX* centers.[4,14] Such energy gain decreases as the size of the nanocrystal increases. Since the impurity state in the *DX* configuration has dominant non-CBM character it does not go up in energy as rapidly as it does at T_d due to quantum confinement (the difference between both energy levels is 1.22 eV, 0.97 eV, and 0.84 eV for the QDs with diameters 1.50 nm, 1.82 nm, and 2.36 nm, respectively[15]). Globally, the Coulombic and electronic structure arguments presented here explain the configuration coordinate diagrams that are shown in the left panel of Fig. 3. In the smaller nanocrystal, the negatively charged fourfold coordinated Si impurity atom placed at T_d shows to be unstable, and the global minimum configuration for the nanocrystal corresponds to the threefold impurity atom placed at C_{3v} (i.e., to the *DX* configuration). As the size of the nanocrystal increases, the difference between the two total-energy minimum configurations is progressively reduced, and finally reversed (in the bulk limit, the only minimum configuration corresponds to the undeformed crystal with T_d symmetry).

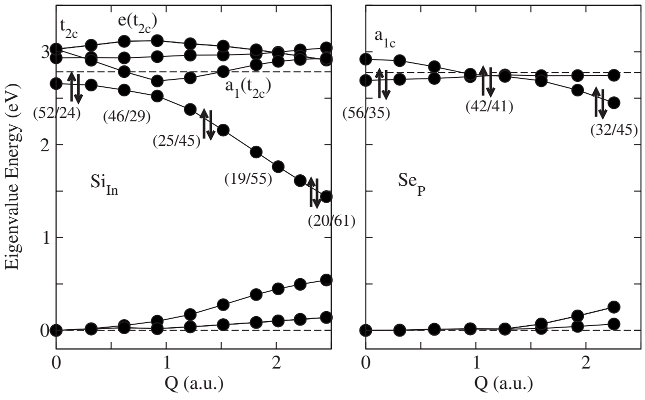

FIG. 5. Electronic structure of the negatively charged Si_{In} (left panel) and Se_P (right panel) InP nanocrystal with diameter 1.50 nm. The arrows represent the impurity state holding the donor-electron pair and the numbers in parentheses its projected s/p characters. Dashed lines correspond to the valence-band maximum and CBM energy levels of the undoped nanocrystal that are used as reference.

The situation we found for the nanocrystals doped at the anion significantly differs from that of those doped at the cation in terms of the formation of *DX* centers (see the right panel of Fig. 3). The configuration coordinate diagrams give a prominent global minimum for the undistorted nanocrystals with T_d symmetry ($Q=0$). In this configuration, the extra electron occupies the impurity donor state (right panel of Fig. 1), similarly to what happens to the undistorted Si_{In}^--doped QDs. Only for the two smallest nanocrystals we found a second metastable minimum that corresponds to the formation of a *DX* center. In this latter configuration a cation In atom that is initially bonded to the impurity Se atom breaks this bond, experiences a displacement along the $\langle 111 \rangle$ direction and finally assumes an interstitial position (right panel of Fig. 4). The ionic distortion that takes place in this process is equivalent to the distortion that occurs in the formation of the *DX* centers for the Si_{In} doped InP-QDs. In this case, the atom displaced from its ideal position is a first neighbor atom of the impurity, rather than the impurity itself.

The driving force for this transformation can also be explained through Coulombic interactions. The fourfold coordinated Se_P^- impurity placed at the tetrahedral position is stable (the negatively charged impurity is now surrounded by cation atoms rather than by anions, so it experiences Coulombic attraction from its first neighbors, and not the repulsion that faces Si_{In}^-). However, the accumulation of extra electronic charge around the impurity introduces some instability in one of the In atoms to which the impurity is bonded, which is surrounded by the ionized impurity and by three anion P atoms. The formation of the *DX* center from the undistorted nanocrystal always implies traversing through high-energy barriers (the computed energy barriers for the QDs with diameters 1.50 nm and 1.82 nm are 0.46 eV and 0.52 eV, respectively).

The different atom that causes the ionic deformation (a cation atom next to impurity and not the impurity itself) also introduces profound changes in the electronic structure of the distorted QDs. When the nanocrystals are doped at the cation, there is an antibonding t_{2c} state located at the impurity. This state accompanies the impurity during the nanocrystal deformation and strongly interacts with the donor state. When the nanocrystals are doped by anion substitution (see the right panel of Fig. 5) there is no such state, the main effect of the ionic deformation being the energy lowering of an empty state (a_{1c}) with same symmetry and CBM character as the impurity state. This state crosses the impurity level and captures the electron-donor pair. As result of this process there is an electronic energy gain but it is negligible when compared to that obtained for the nanocrystals substitutionally doped at the cation. The energy level of the impurity state is lowered 0.24 eV and 0.13 eV in the nanocrystals with diameter 1.50 nm and 1.82 nm, respectively.

In general, our results show that when the nanocrystals are doped by anion substitution the formation of *DX* centers is energetically very unfavorable, and that when this occurs there is no dramatical change in the position of the impurity level within the energy gap. Even though our results were obtained for InP-QDs, the ionic and electronic structure arguments used to interpret them can be generalized to *n*-type III-V nanocrystals with zinc-blende structure. Previous work on $\mathrm{Si}_{\mathrm{Ga}}$-doped GaAs-QDs also gave an increase in the formation energy of the impurity atom and possible stabilization of *DX* centers as result of quantum confinement.[4] We have also checked the effects of using different dopants in the nanocrystals ($\mathrm{Sn}_{\mathrm{In}}$ and S_{P}), finding no essential differences.

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[15] Our results show that there is also some deformation of occupied states with valence-band character, so the electronic energy gain during the defect formation is not strictly that given by the impurity donor state.