Origin of the doping bottleneck in semiconductor quantum dots: A first-principles study

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Doping difficulty in semiconductor nanocrystals has been observed and its origin is currently under debate. It is not clear whether this phenomenon is energetic or depends on the growth kinetics. Using first-principles method, we show that the transition energies and defect formation energies of the donor and acceptor defects always increase as the quantum dot sizes decrease. However, for isovalent impurities, the changes of the defect formation energies are rather small. The origin of the calculated trends is explained using simple band-energy-level models.

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Semiconductor nanocrystals (NCs) have great potential for applications from light-emitting diodes, lasers, and solar cells, to biomedical labeling reagents, because their physical properties such as band gaps could be tailored by controlling their sizes and shapes.[1–7] Application of NCs as optoelectronic devices requires that the materials can be doped so that enough charge carriers can be generated in a controllable manner at the working temperature.[8] Although defect properties have been extensively studied in the past for bulk semiconductors, and various approaches have been proposed to overcome the doping limit,[9] systematic study of the defect properties in NCs is still lacking. For example, it is still not clear how the size of semiconductor NCs affects the defect formation energies and ionization energy levels and how the relative stability of the defects is affected by the NC size.[10]

Experimentally, it has been shown that doping in NCs is more difficult than in bulk semiconductors,[11–15] suggesting possible low dopability in NCs. However, the origin of this doping difficulty is still under debate.[10,15,16] It is not clear if the reduced dopability is energetic, i.e., the formation energy of the dopant increases with the decreasing NC size, or kinetic, i.e., the increased surface area to volume ratio in NCs makes the defect easier to diffuse out of the NCs. To understand this issue, Erwin *et al.*[15] suggested a surface kinetic model to explain the "self-purification" phenomena. Using isovalent Mn doping in CdSe and ZnSe quantum dots (QDs) as examples, they propose that the doping in NCs is controlled by the initial absorption of impurities on the nanocrystal surface during growth; thus, the doping difficulties in NCs are not intrinsic and could be overcome by controlling the surface orientations of the QDs. On the other hand, first-principles calculations[10] show that the formation energy of Si_{Ga}^{0} in GaAs increases significantly when the QD size decreases. Similar results are also observed for donor and acceptor dopings in Si NCs,[17,18] suggesting that self-purification should be an intrinsic effect associated with the increased defect formation energy in small NCs. In a recent study, Dalpian and Chelikowsky[16] also found that for CdSe doped with isovalent Mn_{Cd}, the impurity formation energy increases significantly when the QD sizes are less than 2 nm. However, the origin of the large increase in impurity formation energy for small QDs is not well understood.

To understand the defect formation mechanism in NCs and the origin of the self-purification, we have systematically calculated the formation energies and transition energy levels of donors, acceptors, and isovalent impurities in ZnSe QDs as functions of the QD size. Recently, Mn-doped ZnSe (ZnSe:Mn) QDs with tunable emission in the visible light range have been synthesized.[6,7] The experimental results show that the band gaps of ZnSe NCs can be tuned through doping and that these doped ZnSe QDs can replace CdSe QDs as nontoxic biomedical labels.

Our systematic study revealed that due to the strong quantum-confinement effect in semiconductor QDs, the bonding valence-band maximum (VBM) state shifts downward in energy, whereas the antibonding conduction-band minimum (CBM) state shifts upward in energy. Consequently, the *n*-type and *p*-type defect levels, which are derived mostly from the host CBM and VBM band-edge states, will shift following the respective band-edge states. This leads to an increase in the defect formation energy for defects with electrons in the donor level or holes in the acceptor level and an increase in the transition energy level. However, for isovalent defects, such as Mg_{Zn}- and Mn_{Zn}-doped ZnSe QDs, the change of formation energies as a function of QD size is very small. We also show that the strong *p*-*d* repulsion between the Se *p* orbital and Mn 3*d* orbital is responsible for the experimentally observed reduction of photoluminescence energy in Mn-doped ZnSe QDs.[6,7]

The calculations are performed within the local density approximation[19] as implemented in the VASP code[20] using the projected augmented wave method.[21] The calculated lattice constant of ZnSe is 5.55 Å, in good agreement with experimental value[22] of 5.667 Å. 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.[23,24] In this study, we consider four experimentally accessible dot sizes with diameters of 1.13, 1.53, 1.82, and 2.24 nm, including 35, 87, 147, and 275 atoms, respectively. The calculated band gap E_g of ZnSe at the Γ point is 1.33 eV, which is smaller than the experimental value[22] of 2.82 eV. This band gap error is not expected to have large effect on the calculated relative formation energies.

The defect formation energy and defect transition energy

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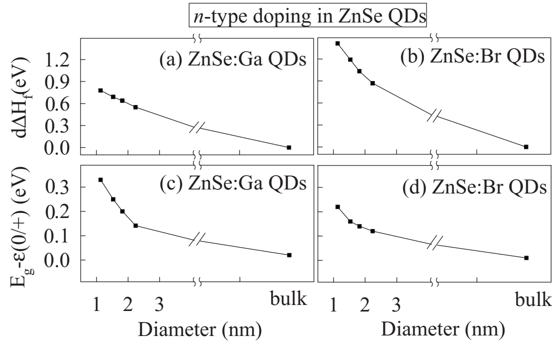

FIG. 1. The relative formation energies $d\Delta H_f$ of neutral donor defects (a) $Ga_{Zn}{}^0$ and (b) $Br_{Se}{}^0$ as a function of the ZnSe QD diameter at $\mu_i=0$. The donor transition energies $E_g-\varepsilon(0/+)$ (i.e., referenced to CBM) of (c) Ga_{Zn} and (d) Br_{Se} as a function of the ZnSe QD diameter.

levels are calculated using the supercell approach, in which a defect is set at the center of a large supercell and periodic boundary conditions are applied. All the internal atoms are relaxed by minimizing the quantum mechanical force and total energy. For charged defects, a uniform charge background is introduced to keep the charge neutrality of the supercell. For the bulk calculation, we use a 512-atom supercell. 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 $E(host)$ 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 and the atomic chemical potentials μ_i,

$$\Delta H_f(\alpha,q) = \Delta E(\alpha,q) + \Sigma n_i\mu_i + qE_F, \tag{1}$$

where $\Delta E(\alpha,q)=E(\alpha,q)-E(host)+\Sigma n_iE_i+q\varepsilon_{VBM}(host)$. Here, the electron Fermi energy E_F is referenced to the VBM of the host, the atomic chemical potential μ_i for the element i is referenced to the elemental solid with energy $E(i)$, n_i is the number of elements i, and q is the number of electrons transferred from the supercell to the reservoirs in forming the defect cell.[10] The defect transition energy level $\epsilon_\alpha(q/q')$, which is the Fermi energy (referenced to VBM) at which the defect has the same energy at charge states q and q', is given by

$$\epsilon_\alpha(q/q') = [\Delta E(\alpha,q) - \Delta E(\alpha,q')]/(q'-q). \tag{2}$$

Donors in ZnSe QDs. Figures 1(a) and 1(b) show the relative formation energy $d\Delta H_f$ (with respect to bulk ZnSe) of neutral donor defects $Ga_{Zn}{}^0$ and $Br_{Se}{}^0$ in ZnSe QDs as a function of the diameter of the QDs, respectively. The diameter $d=\infty$ corresponds to the bulk system. We find that as the size of the QDs decreases, the formation energies of the donor defects (both $Ga_{Zn}{}^0$ and $Br_{Se}{}^0$) increase. The origin of this variation of the formation energy as a function of the QD size can be understood as follows: Due to the strong quantum-confinement effect in semiconductor QDs, the antibonding CBM state moves up in energy. Because the neutral donor level near the conduction-band edge has a strong CBM character, it moves up in energy with the CBM as the QD size decreases [Fig. 2(a)]. Consequently, the defect formation energy of the neutral donor with electrons at the donor level increases as the QD size decreases because more energy is now needed to set an electron on the defect level. However, because this defect level is not a pure CBM state,[10] as the CBM moves up in energy with the decreasing QD size, the energy difference between the defect level and the CBM, thus the (0/+) transition energy level from the CBM also increases. This is consistent with our calculated results shown in Figs. 1(c) and 1(d). The calculated $\varepsilon(0/+)$ transition energy of Ga_{Zn} is shallow at 22 meV below the CBM in the bulk system, in good agreement with experimental value of 27 meV.[22] For Br_{Se}, the calculated value $\varepsilon(0/+) = 12$ meV is also consistent with the experimental data of 29 meV for Cl_{Se} in ZnSe.[22] The large increase of the formation energy (up to 1.41 eV for the smallest QDs studied in this work) and ionization energy indicates that n-type doping will be much more difficult in small QDs than in bulk ZnSe.

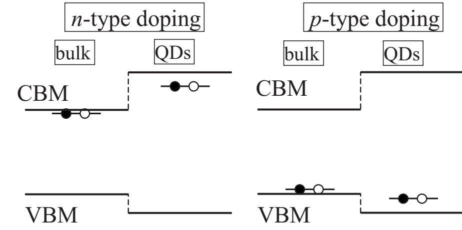

FIG. 2. Schematic illustration of the variation of the single electron energy levels of (a) n-type and (b) p-type dopings in semiconductor QDs.

Acceptors in ZnSe QDs. Figures 3(a) and 3(b) show the formation energy of neutral defects $Cu_{Zn}{}^0$ and $As_{Se}{}^0$ in ZnSe QDs as functions of the QD size. We see that in both cases, the defect formation energies of the neutral defects also increase as the size of the QDs decreases. The origin of this variation of the formation energy as a function of QD size can be understood as follows: Due to the strong quantum-confinement effect in semiconductor QDs, the bonding VBM state moves down in energy. Because the neutral acceptor

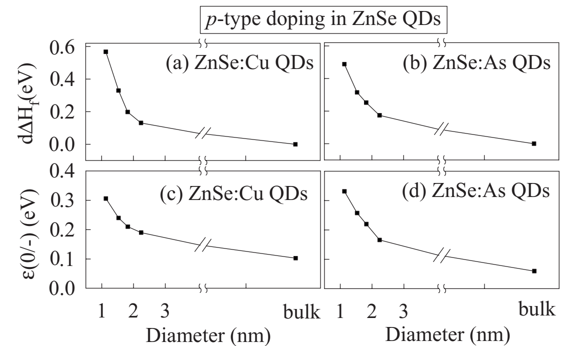

FIG. 3. The relative formation energies $d\Delta H_f$ of neutral acceptor defects (a) $Cu_{Zn}{}^0$ and (b) $As_{Se}{}^0$ as a function of the ZnSe QD diameter at $\mu_i=0$. The transition energies $\varepsilon(0/-)$ (referenced to VBM) of (c) Cu_{Zn} and (d) As_{Se} as a function of the ZnSe QD diameter.

level near the valence-band edge has a strong VBM character, it moves down in energy with the VBM (with respect to vacuum) as the QD size decreases [Fig. 2(b)]. Consequently, the defect formation energy of the neutral acceptor with holes at the acceptor level increases as the QD size decreases because more energy is now needed to remove an electron (create a hole) from the acceptor level. However, because the acceptor state is not a pure VBM state, 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 acceptor transition energy levels deeper. The calculated $\varepsilon(0/-)$ transition energies of Cu_{Zn} and As_{Se} are 102 and 60 meV above VBM in the bulk ZnSe, respectively. The increase of the formation energies and acceptor ionization level in small ZnSe QDs (see Fig. 3) indicates that *p*-type doping will also be much more difficult in small QDs than in bulk ZnSe. However, compared to donor defects, the variation of the formation energy of acceptor defects as a function of QD size is relatively small because the variation of the VBM due to the quantum confinement is relatively smaller than that of the CBM.

Isovalent impurities in ZnSe *QDs*. The above study shows that for neutral donor and acceptor defects with electrons or holes on the defect levels, the defect formation energies increase as the QD sizes decrease. It is very interesting to see if the same trend also applies to the isovalent impurities, which in bulk form can usually be mixed completely with the host material. Experimentally, it is found that S can be easily doped into CdSe QDs, forming stable $CdSe_xS_{1-x}$ QDs.[25] Doping of Mn in CdS, ZnSe, and recently in CdSe also led Erwin *et al.*[15] to suggest that isovalent Mn doping in these II-VI NCs is controlled by kinetic surface effects, not due to the significant increase in the defect formation energy. Our previous study for quasi-isovalent charged impurities such as Si_{Ga}^{+} in GaAs (Ref. 10) and the present study for Ga_{Zn}^{+}, Br_{Se}^{+}, Cu_{Zn}^{-}, and As_{Se}^{-} in ZnSe also found that the variation of the defect formation energies is small, which is consistent with our explanation implied in Fig. 2. However, recent calculation[16] using a high-order finite difference method showed that formation energy of Mn in CdSe increases drastically by more than 1 eV when the QD size is less than 2 nm in diameter. To investigate this further, we calculate here the formation energy of isovalent Mg_{Zn} and Mn_{Zn} substitutional impurities in ZnSe QDs as a function of

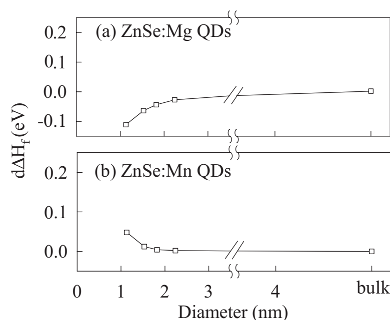

FIG. 4. The relative formation energies $d\Delta H_f$ of the isovalent defects (a) Mg_{Zn} and (b) Mn_{Zn} as a function of the ZnSe QD diameter.

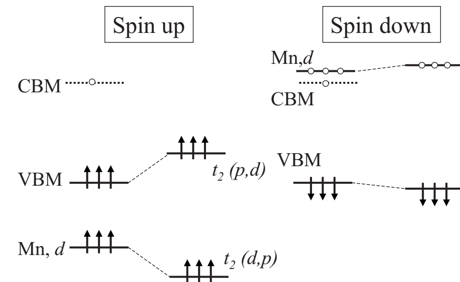

FIG. 5. Schematic plot to show *p*-*d* repulsion between VBM of ZnSe and Mn 3*d* orbital of (a) spin-up and (b) spin-down states in ZnSe:Mn QDs. For clarity, the nonbonding Mn e_d states are not shown.

the QD size. The calculated results are shown in Fig. 4. We find that the change of the formation energy as a function of QD size is small for these isovalent impurities, within 0.1 eV even for the smallest size of QDs. Thus, our results suggest that for isovalent impurity doping in NCs, the doping difficulty should be more closely related to the surface-induced kinetic effect, rather than an intrinsic energetic effect.

For a deeper understanding of the calculated results, we plot in Fig. 5 a schematic model to explain why the formation energy of Mn_{Zn} in ZnSe QDs should be small. When Mn is introduced into ZnSe, it creates a majority spin (spin-up) Mn 3*d* state below the VBM and a minority (spin-down) state above the VBM. The Mn t_{2d} state has the same symmetry as the VBM Se *p*-like state, so the Mn t_{2d} state can couple strongly with the VBM. In the spin-up channel, the *p*-*d* coupling pushes the Mn t_{2d} state down and the VBM up in energy. This level repulsion mixes a significant amount of Mn 3*d* orbital into the VBM wave function, as seen in Fig. 6. However, because both states are fully occupied, this level repulsion, to the first order, does not gain energy. Therefore, despite the quantum confinement moving the VBM level down, making the *p*-*d* coupling stronger in the spin-up channel when the QD size decreases, the effect on the defect formation energy should be small. On the other hand, in the spin-down channel, the Mn 3*d* levels are unoccupied (a similar situation applies to Mg_{Zn} in ZnSe, where Mg *d* states are not occupied). In this case, *p*-*d* repulsion reduces the defect formation energy by pushing down the occupied VBM state. The strength of the *p*-*d* coupling is proportional to $|V_{pd}|^2/(\varepsilon_d-\varepsilon_p)$. When QD size decreases, quantum confine-

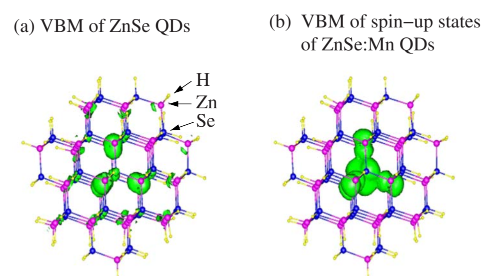

FIG. 6. (Color online) Contour plots of the charge density distribution of (a) VBM state of $Zn_{43}Se_{44}H_{76}$ QD and (b) spin-up VBM state of $Zn_{42}Se_{44}Mn_1H_{76}$ QD. Mn atom is at the center of QDs.

ment moves the VBM down, making p-d coupling weak because of the increase in $(\varepsilon_d - \varepsilon_p)$. However, reduced QD size also increases the coupling matrix element $|V_{pd}|$ due to the increased overlap between the Mn d and anion p states. These two effects partially cancel each other, so the variation of the relative defect formation energy due to the p-d coupling is small and can be either positive or negative. The above analysis is consistent with our calculated results.

Moreover, the p-d repulsion between the Se p orbital and occupied Mn $3d$ orbital creates a deep level inside the band gap, thus effectively reducing the band gap when the Mn concentration is high. The exact position of the defect level depends on the Mn concentration and the size of the ZnSe QDs. Therefore, doping ZnSe QDs with transition metals such as Mn provides another approach to tune the band gap; thus, the emission colors can be controlled in optoelectronic applications such as biomedical labels.[6,7]

In summary, using first-principles total-energy and band-structure calculations, we have investigated the origin of doping difficulty in semiconductor QDs. We show that due to quantum confinement, the defect (acceptor or donor) transition energies always increase as the sizes of QDs decrease, as do the formation energies of donor or acceptor defects with electrons or holes on the defect levels, respectively. However, for isovalent defects, such as Mg_{Zn} and Mn_{Zn} doped in ZnSe QDs, the change of the formation energies should be small. These results suggest that for donor and acceptor defects, the origin of doping difficulty is most likely due to energetic effect, whereas for isovalent defect, it is most likely due to kinetic effects. We also show that due to strong p-d repulsion between the Se p orbital and occupied Mn $3d$ orbital, Mn doping in ZnSe QDs can be used to tune the effective band gap, and thus, the emission peak, in agreement with experimental observations.

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