Effects of charged defects on the electronic and optical properties of self-assembled quantum dots

Ranber Singh and Gabriel Bester
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany.
(Dated: May 5, 2014)

We investigate the effects of point charge defects on the single particle electronic structure, emission energies, fine structure splitting and oscillator strengths of excitonic transitions in strained In$_{0.6}$Ga$_{0.4}$As/GaAs and strain-free GaAs/Al$_{0.3}$Ga$_{0.7}$As quantum dots. We find that the charged defects significantly modify the single particle electronic structure and excitonic spectra in both strained and strain-free structures. However, the excitonic fine structure splitting, polarization anisotropy and polarization direction in strained quantum dots remain nearly unaffected, while significant changes are observed for strain-free quantum dots.

PACS numbers: 73.21.Hb,42.50.-p,73.21.La,78.67.Hc

I. INTRODUCTION

Point charge defects in semiconductors modify their properties, including their electronic structure, trapping and recombination rates for electrons and holes, and luminescence quenching. Point defects in semiconductors have been studied extensively with the aim to use their properties for defect engineering. Understanding the properties of point defects is important in studying the electrical and optical properties of semiconductors.

To date, little is known about the influence of point defects on the electronic structure and optical properties of self-assembled semiconductor quantum dots (QDs) grown epitaxially by the Stranski-Krastanow growth mode. These type of QDs provide a quantum system which can be engineered to have a wide range of desired properties and provide a rather unique opportunity to investigate various effects known from atomic physics, in a solid state environment. However, their electronic structure and optical properties can be altered by the presence of defects inside the QDs or in the surrounding barrier. The defects responsible for the electron (hole) trapping in III-V semiconductor heterostructures are the positively (negatively) charged acceptor (donor)-like defects such as vacancies, interstitial or substitutional defects. These defects in strained In(Ga)As/GaAs and strain-free GaAs/Al(Ga)As QDs may develop during the growth process. The negatively charged donor-like substitutional Si defect in GaAs QDs are predicted to be stable. A point charge may also get trapped at a defect site during an optical or electrical measurement. Charged defects inside a QD or in the surrounding region may change the depth and symmetry of the confining potential quite significantly affecting the electronic and optical properties of the QD. The influence of these defects on the optical properties have been shown only in few cases, namely for self-assembled Ge/Si, CdSe/ZnSe, and InGaAs/AlGaAs QDs. For colloidal QDs, on the other hand, the phenomena has been extensively investigated. The so-called blinking, is often attributed to the trapping of carriers into defect states on the surface or the surrounding matrix and represents a severe limitation for many potential applications.

For self-assembled QDs, we may speculate that charged defects may be responsible for the large spread of the excitonic fine structure splitting (FSS), polarization direction and polarization anisotropy in strained In(Ga)As and strain-free GaAs/Al(Ga)As QDs. We use an atomistic empirical pseudopotential description and configuration interaction. The charged defects are modeled at the level of the hydrogenic effective mass description (neglecting central cell effects). We find that the charged defects significantly modify the electronic structure and excitonic spectra in both strained and strain-free QDs. However, the FSS, polarization anisotropy and polarization direction in strained QDs remain nearly unaffected, while in strain-free QDs there are significant changes in these quantities.

II. COMPUTATIONAL DETAILS

We consider impurity defects given as, $V = \frac{\pm 1}{\epsilon |\mathbf{r} - \mathbf{r}_0|}$, following hydrogenic effective mass theory and ignoring the central cell effects, where $\epsilon$ is the dielectric constant of the material composing the QD and $\mathbf{r}_0$ is the position of the impurity. The positively ($\oplus$) and negatively ($\ominus$) charged point defects are placed at different locations shown schematically in Fig. 1. We used a lens-shaped QD with cylindrical base of 25.2 nm diameter and 3.5 nm height. We relax the atomic positions within the simulation cell to the minimum strain energy using the valence force field method. The single particle orbitals and energies of the QD are calculated by using the atomistic empirical pseudopoten-
The energetic splitting between different defect configurations in In\(_0\)Ga\(_{0.4}\)As/GaAs QDs and strain-free GaAs QDs in response to the charged defects are calculated from the atomic wave functions as shown in Ref\([30]\) and the correlated excitonic states are calculated by the configuration interaction (CI) approach\([31]\). For the CI calculations we use all possible determinants constructed from the twelve lowest energy electron and twelve lowest hole states (spin included), thus accounting for correlations.

### III. RESULTS AND DISCUSSION

#### A. Single particle states

The single particle energies of electron (\(e_{0.1,2}\)) and hole (\(h_{0.1,2}\)) states are given in Figs. 2 and 3 for the different defect configurations in In\(_{0.6}\)Ga\(_{0.4}\)As/GaAs and GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As QDs. We observe significant changes in the electronic structure of both strained In\(_{0.6}\)Ga\(_{0.4}\)As and strain-free GaAs QDs in response to the charged defects. The energetic splitting between \(S\) and \(P\) states is significantly modified and the energies of electron and hole states blue-shift (red-shift) for negatively (positively) charged defects. This is due to the fact that the negative defects repel (attract) an electron (hole) and accordingly for the positive defects. The energetic splittings between the electron \(P\) states (\(e_{1,2}\)) and holes (\(h_{1,2}\)) increase when the defects are placed along the [1\(\bar{1}\)0] crystallographic direction because it increases the inequivalence between the [110] and [1\(\bar{1}\)0] directions. In strain-free GaAs QDs there is a larger splitting of the \(P\) hole states for the negative defects placed at positions 1 and 2. This is due to the increase of light-hole character in response to the delocalization of the wave functions in \(z\)-direction as will be demonstrated next. The decomposition of the S hole state into light-hole (LH) and heavy-hole (HH) components is given in Table 1. The negative point defects ⊖ at positions 1 and 2 lead to an increase of the LH-component, while the positive point defects ⊕ at the same positions induce a reduction of the LH-component. This can be understood from the reduced and increased Z-component of the hole wave functions.

The isosurfaces enclosing 75% of the probability density of electron and hole states in strained In\(_{0.6}\)Ga\(_{0.4}\)As/GaAs and strain-free GaAs QDs with different point charge configurations are shown in Fig. 4.
TABLE I: Decomposition of $S$ hole states into LH and HH components and Coulomb integrals of hole-hole ($J_{hh}$), hole-electron ($J_{he}$) and electron-electron ($J_{ee}$) interactions for the $S$ states. The sign ‘+’ (‘−’) indicate positively (negatively) charged defect. The position of defects (1, 2, 3) are defined in Fig. 1.

| QD          | defect | $S$ hole state | Coulomb integrals |  |
|-------------|--------|----------------|-------------------|---|
|             |        | HH  | LH  | $J_{hh}$ | $J_{he}$ | $J_{ee}$ |  |
| GaAs        | none   | 89.48 | 09.33 | 25.97   | 24.86   | 23.94   |  |
|             | $1^{−}$  | 84.50 | 13.90 | 35.37   | 26.11   | 22.26   |  |
|             | $2^{−}$  | 84.16 | 14.21 | 35.61   | 26.15   | 22.28   |  |
|             | $3^{−}$  | 84.77 | 13.76 | 29.50   | 20.54   | 24.01   |  |
|             | $1^{+}$  | 90.73 | 08.10 | 20.65   | 22.15   | 25.98   |  |
|             | $2^{+}$  | 90.22 | 08.61 | 20.78   | 22.26   | 25.98   |  |
|             | $3^{+}$  | 88.14 | 10.65 | 26.17   | 23.82   | 23.89   |  |
| In$_{0.6}$Ga$_{0.4}$As | none   | 94.00 | 02.46 | 24.68   | 20.95   | 18.61   |  |
|             | $1^{−}$  | 92.70 | 03.31 | 29.91   | 21.03   | 17.35   |  |
|             | $2^{−}$  | 92.87 | 03.21 | 29.34   | 21.00   | 17.40   |  |
|             | $3^{−}$  | 93.90 | 02.52 | 24.52   | 19.95   | 18.64   |  |
|             | $1^{+}$  | 94.34 | 02.25 | 21.13   | 20.12   | 20.05   |  |
|             | $2^{+}$  | 94.36 | 02.23 | 21.26   | 20.29   | 19.97   |  |
|             | $3^{+}$  | 93.86 | 02.56 | 25.10   | 20.30   | 18.67   |  |

The defect placed along the [110] crystal direction (position 3) breaks the symmetry, which is clearly evident from the spacial distribution of the hole states. The negative defect placed along the [110] crystal direction changes the orientation of the $P$ states as compared to the case of the defect-free QD. The negative (positive) defect at position 3 favors hole (electron) $P$ state along the [110] crystal direction and the effect is so large as to reverse the energetic order of the states. Similar effects are observed for electrons in strain-free GaAs/Al$_{0.3}$Ga$_{0.7}$As QDs (not shown). The spatial extent of the hole states in the GaAs/Al$_{0.3}$Ga$_{0.7}$As QD deviates significantly from the nearly single-band case of the InGaAs/GaAs QD. This is a consequence of the strong band mixing observed in the GaAs QD and will be further discussed in section III.C. We observe that the negative defects lead to a contraction of the wave functions, while the positive point charges close to the QD center (position 1 and 2) repel the wavefunctions.

The Coulomb integrals for hole-hole ($J_{hh}$), hole-electron ($J_{he}$) and electron-electron ($J_{ee}$) interactions between the $S$ states are given in Table I. The increase (decrease) in the magnitude of the Coulomb integrals $J_{hh}$ and $J_{ee}$ indicates an increase (decrease) in the localization of the hole and electron states, respectively. For the GaAs QD the presence of a negative charge increases the $J_{hh}$ integrals by a large value of about 10 meV. The $J_{ee}$ integrals are thereby reduced by only around 1 meV. This is related to the rather different effective masses of the electron and the hole in this material. The hole state has an increased ability to localize in the additional Coulomb potential created by the charged defect, compared to the electron. The changes observed in the $J_{eh}$ Coulomb integrals follow qualitatively the changes observed for the holes, i.e., for a negative defect, the magnitude of integrals increase. The same trends are observed for the InGaAs QD, but with a generally smaller magnitude.

B. Exciton fine structure splitting and polarization

The emission energy, FSS, polarization direction and polarization anisotropy of neutral excitons in In$_{0.6}$Ga$_{0.4}$As/GaAs and GaAs/Al$_{0.3}$Ga$_{0.7}$As QDs is tabulated in Table II. The polarization anisotropy is defined as $(I_1-I_2)/(I_1+I_2)$, where $I_1$ and $I_2$ are, respectively, the intensities along major and minor axis of the elliptically polarized total emission of two neutral bright
TABLE II: Emission energy, FSS, polarization anisotropy and polarization direction with respect to the [110] crystal direction of neutral exciton. The sign ‘+’ (‘-’) indicate positively (negatively) charged defect. The position of the defects (1, 2, 3) are defined in Fig.1.

| QD                  | defect | energy (eV) | FSS (µeV) | polarization | polarization direction (°) | (%) |
|---------------------|--------|-------------|-----------|--------------|----------------------------|-----|
| none                | 1.700  | 12.2        | 89.8      | 0             | 7.5                        |
| 1                   | 1.692  | 04.4        | 89.5      | 04.5         |                            |
| 2                   | 1.692  | 11.9        | 00.1      | 03.5         |                            |
| 3                   | 1.699  | 13.9        | 00.1      | 06.5         |                            |
| 1′                  | 1.700  | 17.1        | 89.9      | 11.9         |                            |
| 2′                  | 1.700  | 22.7        | 89.9      | 14.9         |                            |
| 3′                  | 1.699  | 17.9        | 90.0      | 12.2         |                            |
| GaAs                | none   | 1.237       | 4.2       | 2.4          | 0.2                       |
| 1′                  | 1.229  | 3.5         | 3.5       | 0.1          |                            |
| 2′                  | 1.230  | 3.7         | 3.5       | 0.1          |                            |
| 3′                  | 1.236  | 3.8         | 0.5       | 1.2          |                            |
| 1′′                 | 1.239  | 5.0         | 2.2       | 0.1          |                            |
| 2′′                 | 1.238  | 4.7         | 1.8       | 0.1          |                            |
| 3′′                 | 1.236  | 4.3         | 2.4       | 0.1          |                            |

FIG. 5: Absorption spectra of neutral excitons (X) and charged excitons (X+, X−) in In0.6Ga0.4As/GaAs QDs. The positions of the defects are defined (1, 2, 3) in Fig.1. The exciton lines have interchanged (anticrossed\textsuperscript{32}). We conclude, that the position of the defect along the symmetry axis (through the center of the dot, i.e., the z-axis) and the vertical electric field it creates, has a significant influence on the FSS and is even able to “reverse” it. Strong effects on the vertical electric fields on the FSS have been observed previously\textsuperscript{33}. The non-zero polarization anisotropy in GaAs QDs is due to large LH-HH mixing. We also notice that the polarization direction in GaAs QDs with cylindrical symmetry is not always along the [110] crystallographic axis. This is due to the atomistic random nature of the barrier composition and hence the interface of the QD.

C. Excitonic spectra

The absorption spectra of neutral and charged excitons in InGaAs and GaAs QDs with different point charge defect configurations are given in Fig.5 and 6. The SS, PP and DD labels characterize the different orbital characters of the electron and hole states involved in the optical transition. The actual orbital S, P, D character of the hole wave functions for the GaAs QD is given in Table III. It becomes clear that strong deviations from orbitally pure states exist in GaAs. The states can hardly be classified as “S”, “P”, “D” as they have a mostly mixed char-
FIG. 6: Absorption spectra of neutral excitons (X) and charged excitons (X\(^+\), X\(^-\)) in GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As QDs. The positions of the defects are defined (1, 2, 3) in Fig[4] The labels SS, PP and DD refer to the transitions from the electron S, P, D states, respectively, to the hole states h\(_{0,1,2,3,4,5}\). Since the hole states have a heavily mixed orbital character (see Table III), transitions to all of them are possible, leading to a high multiplicity of peaks.

TABLE III: Decomposition of the atomistic hole wave functions in a GaAs QD into bulk Γ point Bloch functions times envelope functions: \(\Psi_n(r) = \sum_{\alpha} \phi_\alpha(r) \psi_n(r)\) where \(\phi_\alpha\) is the Bloch function of band \(\alpha\) and \(\psi_n\) is the corresponding envelope function. The decomposition factors tabulated here are the norm of the envelope functions for the three dominant valence bands \(x\), \(y\) and \(z\). These bands are labelled by their axial angular momentum values \(j = \frac{3}{2}\) for \((x+iy)/\sqrt{2}\), \((x-iy)/\sqrt{2}\); \(j = \frac{1}{2}\) for \((x-iy)/\sqrt{2}\), \((x+iy)/\sqrt{2}\); and \(j = \frac{1}{2}\) for \(z\). Each envelope function contains a combination of angular momenta (S, P, D), given in percent.

| label | norm of the envelope function |
|-------|-------------------------------|
|       | \(j = \frac{3}{2}\) | \(j = \frac{1}{2}\) | \(j = \frac{1}{2}\) |
|       | S | P | D | S | P | D | S | P | D |
| \(h_0\) | 83.1 | 23.0 | 3.1 | 0.3 | 0.6 | 0.0 | 0.5 | 2.0 | 1.1 |
| \(h_1\) | 3.6 | 40.2 | 6.4 | 4.5 | 7.4 | 0.4 | 8.2 | 13.6 | 0.7 |
| \(h_2\) | 3.5 | 15.0 | 15.6 | 11.9 | 4.4 | 0.2 | 22.4 | 8.1 | 0.4 |
| \(h_3\) | 1.5 | 52.5 | 3.0 | 0.2 | 4.2 | 1.1 | 0.4 | 7.2 | 2.9 |
| \(h_4\) | 34.0 | 5.0 | 2.6 | 0.5 | 1.6 | 9.9 | 0.7 | 3.1 | 18.4 |
| \(h_5\) | 7.3 | 15.9 | 17.8 | 2.2 | 5.2 | 2.1 | 3.4 | 10.8 | 3.3 |

ACKNOWLEDGMENTS

We would like to acknowledge financial support by the BMBF (QuaHL-Rep, Contract No. 01BQ1034).
E. G. Seebauer and M. C. Kratzer, Materials Science and Engineering: R: Reports 55, 57 (2006).

P. Michler, A. Kiraz, C. Becher, W. V. Schoenfeld, P. M. Petroff, L. D. Zhang, E. Hu, and A. Imamoglu, Science 290, 2252 (2000).

S. Cortez, O. Krebs, S. Laurent, M. Senes, X. Marie, P. Voisin, R. Ferreira, G. Bastard, J. M. Gerard, and T. Amand, Phys. Rev. Lett. 89, 207401 (2002).

X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir, and S. Weiss, Science 307, 538 (2005).

B. D. Gerardot, D. Brunner, P. A. Dalgarno, P. Ohberg, S. Seidl, M. Kroner, K. Karrai, N. G. Stoltz, P. M. Petroff, and R. J. Warburton, Nature 451, 441 (2008).

R. B. Patel, A. J. Bennett, I. Farrer, C. A. Nicoll, D. A. Ritchie, and A. J. Shields, Nat. Photon. 4, 632 (2010).

M. Kroner, A. O. Govorov, S. Remi, B. Biedermann, S. Seidl, A. Badolato, P. M. Petroff, W. Zhang, R. Barbour, B. D. Gerardot, et al., Nature 451, 311 (2008).

J. Li, S.-H. Wei, and L.-W. Wang, Phys. Rev. Lett. 94, 185501 (2005).

T. Nguyen-Duc, V. L. Thanh, V. Yum, P. Boucaud, D. Bouchier, O. Schmidt, and J. Derrien, Thin Solid Films 508, 207 (2006).

H. Kamada and T. Kutsuwa, Phys. Rev. B 78, 155324 (2008).

A. L. Efros and M. Rosen, Phys. Rev. Lett. 78, 1110 (1997).

V. I. Klimov, A. A. Mikhailovskiy, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Science 287, 1011 (2000).

B. Mahler, P. Spinicelli, S. Buil, X. Quelin, J.-P. Hermier, and B. Dubertret, Nat. Mater. 7, 659 (2008).

S. Seidl, B. D. Gerardot, P. A. Dalgarno, K. Kowalik, A. W. Holleitner, P. M. Petroff, K. Karrai, and R. J. Warburton, Physica E: Low-dimensional Systems and Nanostuctures 40, 2153 (2008).

J. D. Plumhof, V. Krápek, L. Wang, A. Schliwa, D. Bimberg, A. Rastelli, and O. G. Schmidt, Phys. Rev. B 81, 121309 (2010).

R. Seguin, A. Schliwa, S. Rodt, K. Potschke, U. W. Pohl, and D. Bimberg, Phys. Rev. Lett. 95, 257402 (2005).

C.-H. Lin, W.-T. You, H.-Y. Chou, S.-J. Cheng, S.-D. Lin, and W.-H. Chang, Phys. Rev. B 83, 075317 (2011).

N. Porras-Monteregno and S. T. Pérez-Merchancano, Phys. Rev. B 46, 9780 (1992).

S. T. Pantelides, Rev. Mod. Phys. 50, 797 (1978).

A. S. Martins, J. G. Menchero, R. B. Capaz, and B. Koiller, Phys. Rev. B 65, 245205 (2002).

P. N. Keating, Phys. Rev. B 145, 637 (1966).

A. J. Williamson, L.-W. Wang, and A. Zunger, Phys. Rev. B 62, 12963 (2000).

L.-W. Wang and A. Zunger, Phys. Rev. B 59, 15806 (1999).

G. Bester, S. Nair, and A. Zunger, Phys. Rev. B 67, 161306 (2003).

A. Franceschetti, H. Fu, L.-W. Wang, and A. Zunger, Phys. Rev. B 60, 1819 (1999).

R. Singh and G. Bester, Phys. Rev. Lett. 104, 196803 (2010).

A. J. Bennett, M. A. Pooley, R. M. Stevenson, M. B. Ward, R. B. Patel, A. B. de la Giroday, N. Skold, I. Farrer, C. A. Nicoll, D. A. Ritchie, et al., Nat. Phys. 6, 947 (2010).