Electronic states of (InGa)(AsSb)/GaAs/GaP quantum dots

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Detailed theoretical studies of the electronic structure of (InGa)(AsSb)/GaAs/GaP quantum dots are presented. This system is unique since it exhibits concurrently direct and indirect transitions both in real and momentum space and is attractive for applications in quantum information technology, showing advantages as compared to the widely studied (In,Ga)As/GaAs dots. We proceed from the inspection of the confinement potentials for \( k \neq 0 \) and \( k = 0 \) conduction and \( k = 0 \) valence bands, through the formulation of \( k \cdot p \) calculations for \( k \)-indirect transitions, up to the excitonic structure of \( \Gamma \)-transitions. Through this process we compare the results obtained for dots on both GaP and GaAs substrates enabling us to make a direct comparison to the (In,Ga)As/GaAs quantum dot system.

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INTRODUCTION

Monolithic integration of III-V compounds with Si-technology is one of the key challenges of future photonics [1]. The problems caused by the large lattice mismatch between Si and typical emitter materials based on GaAs or InP substrates, can be avoided to a large extent by employing a pseudomorphic approach, i.e. growing almost lattice matched compounds on Si. The III-V binary compound with the lattice constant closest to Si is GaP (0.37% lattice mismatch at 300K). GaP is an indirect semiconductor, not seen as a useful laser material. It might serve however as a matrix for more appropriate material combinations. The initially obvious choice of employing InGaP as active material fails due to the borderline type-I/II nature of the bandoffset to GaP [2]. InGaAs/GaP by contrast features a type I lineup and triggered a fair amount of research, both experimental and theoretical in nature [3,9]. The main issue with this material combination is the large lattice mismatch and the resulting large strain in the InGaAs active material, possibly leading to direct - indirect crossover of the ground state transition. Fukami et al. [10] was the first to evaluate the necessary fraction of In for a direct electron-hole ground state transition using model-solid theory for InGaAsN/GaP. Further theoretical insight was provided by the work of Robert et al. [11,12] who first employed a mixed \( k \cdot p \) / tight-binding simulation predicting a direct-indirect crossover at about 30% In-content for larger InGaAs/GaP QDs. For smaller QDs he predicted an even larger In content for the direct transition in reciprocal space.

In the present work we take the next step and assess the role of additional antimony incorporation leading to In\(_{1-x}\)Ga\(_x\)As\(_y\)Sb\(_{1-y}\)/GaP QDs - based on the experimental works of Sala et al. [14]. Not only will we look at its suitability as optoelectronic material but also - as discussed by Sala et al. [14] - as material for nano-flash memories. The secret for successful growth of such InGaAsSb/GaP QDs by MOCVD constitutes a 3 ML GaAs interlayer on top of the GaP matrix material, thus reducing the surface energy and enabling QD formation [15], which will be carefully considered in the following simulations. The theoretical model employed by us follows previous work [16,17]: a 3D \( 8 \)-band- \( k \cdot p \) model is used for electronic states around the \( \Gamma \)-point and an effective mass model for off-\( \Gamma \)-states such as \( L \)- and \( X \)-states. Strain is accounted for by using continuum elasticity [18] and piezoelectricity is considered up to second order [19,21]. Coulomb interaction is included via the configuration interaction model, thus, accounting for exchange and correlation effects [22,24].

The eight- (six-) fold symmetry of \( L \) (\( X \)) bulk Bloch waves translates into four- (three-) \( L \) (\( X \)) envelope functions for quasiparticles in QDs due to the symmetry along [001] (inversion symmetry). We denote the resulting envelope wavefunctions \( L_{[110]} \), \( L_{[1\bar{1}0]} \), \( L_{[1\bar{1}0]} \), and \( L_{[100]} \) \( (X_{[100]} \), \( X_{[010]} \), and \( X_{[001]} \)). The degeneracy of envelopes for \( L_{[110]} \), \( L_{[1\bar{1}0]} \), \( L_{[1\bar{1}0]} \), and \( L_{[100]} \), or \( X_{[100]} \), \( X_{[010]} \), and \( X_{[001]} \) bands is lifted in real dots due to structural imperfections (e.g. shape, composition) or by external perturbations (e.g. electric, magnetic, or strain fields) and we thus distinguish between these bands in the following and study also the effects of degeneracy lifting. We carefully choose three exemplary points A, B, C, and D as seen in Fig. [1] and Tab. [2] that exhibit certain specific properties of our system, which will be discussed further in the the body of the paper.
The paper is organized as follows: we start with inspection of the confinement potentials \{(a)\} followed by the formulation of the method for single-particle calculations based on the combination of one- and eight-band \(k\cdot p\) approximation \{see top inset of (b) and Fig. 3\}. Using that we analyze the electron and hole probability densities and eigen energies, respectively \{(b)\}. Based on these results we then inspect the electron-hole Coulomb integrals for \(\Gamma\)-point states and derive information on type-I/II behaviour. Finally, we study the fine-structure and emission properties of excitons consisting of \(\Gamma\)-electrons and holes.

**TABLE I.** Ga and As concentrations corresponding to points A, B, C, and D in Fig. 1.

| Point | \(c(\text{Ga})\) | \(c(\text{As})\) |
|-------|-----------------|-----------------|
| A     | 0.2             | 0.2             |
| B     | 0.8             | 0.2             |
| C     | 0.8             | 0.8             |
| D     | 0.2             | 0.8             |

**FIG. 1.** In-plane compressive hydrostatic strain \((\epsilon_{xx} + \epsilon_{yy})\) and ratio of the induced vertical polarizations \((p_{2nd}/p_{1st})\) are shown in the top and bottom panels, respectively. The concentrations are given either for \(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{Sb}_{1-y}\) on GaP (left column) or on GaAs (right column) substrates. Notice the pronounced compressive stress for small \(x\) and \(y\) (i.e. towards pure \(\text{InSb}\)) and more than seven-fold larger importance of 2nd-order piezoelectricity compared to 1st-order for structures grown on GaP. The capital letter A, B, C, and D mark the concentrations listed in Tab. I. For the interpolation scheme between different constituents used here see Eqs. (1a) and (1b).

**FIG. 2.** (a) Band edges of \(\Gamma\), L, \(X_{[001]}\), \(X_{[100]/[010]}\) electron and \(\Gamma\) hole bands for \(\text{In}\) and \(\text{Ga}\) compositions marked as A in Tab. I. The corresponding single-particle ground state eigen energies are indicated by horizontal lines and correspond in panel (b) to side views of the probability densities of the envelope functions. QD body in (b) is indicated by grey objects. The top panel in (b) shows the method of calculation of \(k = 0\) and \(k \neq 0\) states in our theory. The vertical line between \(\Gamma\) electron and hole states marks the recombination between these states with radiative lifetime of \(\tau_{\text{life}} = 1\) ns. In panel (c) we give the side view of the simulated \(\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{Sb}_{1-y}/\text{GaAs}/\text{GaP}\) QD. The shape of QD is a truncated cone with height \(h = 2.5\) nm and base (top) diameter \(d_b = 15\) nm (\(d_t = 8\) nm). The QDs are positioned on a 5 ML thick IL of pure GaAs and the whole structure is embedded in GaP.

**METHOD OF CALCULATION**

**FIG. 3.** Schematics of the modeling procedure applied in this work.

Figure 3 shows an outline of the modeling procedure
employed in this paper. It starts with an implementation of the 3D QD model structure (size, shape, chemical composition), and carries on with the calculation of strain and piezoelectricity. The resulting strain and polarization fields then either enter the eight-band $k \cdot p$ Hamiltonian for states located around the Brillouin-center ($\Gamma$-point) or the effective-mass Hamiltonian for those emerging off-center such as L- and X-point states. Solution of the resulting Schrödinger equations yields electron and hole single-particle states both at the $\Gamma$- as well as at X- and L-points. Coulomb interaction is accounted for by employing the conformation interaction (CI) method including dipole-dipole interaction. Finally, optical properties such as absorption spectra, capture cross sections, or lifetimes can be calculated.

Choice of model structure

The morphology of our model QD is related to the works of Stracke and Sala [14,15,25,26]: The whole structure is grown on GaP substrate with an IL between works of Stracke and Sala [14, 15, 25, 26]: The whole or lifetimes can be calculated. The single-particle states for L- and X-electrons are calculated using the eight-band $k \cdot p$ model, detailed in the next paragraph.

Single particle states

Owing to the choice of materials and the arising large strain values, the CB-electronic ground state is in general not a $\Gamma$-state. Hence, we resort to a hybrid approach [10] in that, we calculate the $\Gamma$-states using the eight-band $k \cdot p$ model and the L- and X-states using the effective mass model, both including strain and piezoelectricity. All the preceding steps of the calculation are done using the nextnano++ simulation suite [28] [30].

Eight band $k \cdot p$ theory for $\Gamma$-states

The energy levels and wavefunctions of zone-center electron and hole states are calculated using the eight-band $k \cdot p$ model, which was originally developed for the description of electronic states in bulk material [31] – [33]. In the context of heterostructures, the envelope function version of the model has been applied to quantum wells (QWs) [34], quantum wires [35], and QDs [36 – 40]. Details of the principles of our implementation are outlined in Ref. [35, 40].

This model enables us to treat QDs of arbitrary shape and material composition, including the effects of strain, piezoelectricity, VB mixing, and CB-VB interaction. The strain enters our model via deformation potentials as outlined by Bahder [41]. Its impact on the local bandedges as a function of the QD geometry will be discussed further below.

Due to the limited number of Bloch functions used for the wave function expansion, the results of the eight-band $k \cdot p$ model are restricted to close vicinity of the Brillouin zone center. Therefore, we separately calculate off-center states using the effective mass model, detailed in the next paragraph.

Effective mass theory for L- and X-states

The single-particle states for L- and X-electrons are obtained within the envelope function method based on effective mass approximation, i.e., the following equation...
direction of the conduction band.

\[ H^{L,X} F(r) = EF(r), \]

(2)

where \( E \) and \( F(r) \) are the eigenenergy and the envelope function, respectively, and \( H^{L,X} \) is given by

\[ H^{L,X} = -\frac{\hbar^2}{2} \nabla \cdot \left( \frac{1}{m^*(r)} \nabla \right) + E_c^L(r) + \psi_{\text{ext}}(r). \]

Here \( E_c^L(r) \) is the positionally dependent bulk conduction band energy for L or X point, \( \psi_{\text{ext}}(r) \) is the external potential induced by, e.g., elastic strain, and \( \nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)^T \) is the gradient. The effective mass parameter \( m^*(r) \) is given by

\[ m^*(r) = [m_1^*(r) - m_2^*(r)] k_0^T k_0 + m_3^*(r) 1_{3 \times 3}, \]

(4)

where \( m_1^*(r) \) and \( m_2^*(r) \) are positionally dependent longitudinal and transversal effective masses, respectively, \( k_0 = (100) \) (\( k_0 = (111)/\sqrt{3} \) for X-point (L-point) of the Brillouin zone and \( 1_{3 \times 3} \) is 3 \times 3 the identity matrix.

**Strain and its effect on local bandedges**

As the impact of strain on the confinement is comparable to the band offsets at the heterojunctions, the wavefunctions and energies are very sensitive to the underlying strain distribution. The natural choice of appropriate strain model in the context of multiband k-p theory is the continuum elasticity model [18]. Its pros and cons compared to valence-force-field like models are discussed in a number publications [20, 38, 42]. The magnitude of the strain induced band-shifts is determined by the material dependent deformation potentials [43, 44]. For the conduction band \( \Gamma \)-point as well as for the valleys at the X-point and the L-point the strain induced energy shift is given by [43]:

\[ E_c^L(k_0, \varepsilon) = E_c^L(k_0) + \Xi_d^{tr}(\varepsilon) + \Xi_u^u(k_0, \varepsilon, k_0) \]

(5)

with the absolute \( \Xi_d^d \) and the uniaxial \( \Xi_u^u \) deformation potentials; \( \varepsilon \) is the strain.

Evaluating Eq. (5) for the strain conditions at the vertical centerline of our QD with \( \varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = 0 \) one arrives at:

\[ E_c^L([000], \varepsilon) = E_c^L + a_{cu}^L \varepsilon_{yy}, \]

\[ E_c^L([111], \varepsilon) = E_c^L + a_{cu}^L \varepsilon_{xx} + \frac{1}{3} a_{cu}^L (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \]

\[ E_c^X([100], \varepsilon) = E_c^X + a_c^L \varepsilon_{xx} + a_c^X (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}), \]

\[ E_c^X([010], \varepsilon) = E_c^X + a_c^L \varepsilon_{yy} + a_c^X (\varepsilon_{xx} + \varepsilon_{yy}), \]

\[ E_c^X([001], \varepsilon) = E_c^X + a_c^L \varepsilon_{zz} + a_c^X (\varepsilon_{xx} + \varepsilon_{zz}). \]

where \( a_c \) being the absolute deformation potential and \( a_{cu} \) the uniaxial shear deformation potential in [100]-direction of the conduction band.

The expression for \( E_c^X([111], \varepsilon) \) is identical for all \( L \)-points, whereas a strain dependent splitting occurs between the energies of \( E_c^X([100], \varepsilon) \), \( E_c^X([010], \varepsilon) \) and \( E_c^X([001], \varepsilon) \). At the QD’s centerline, however, \( \varepsilon_{xx} = \varepsilon_{yy} \) holds and the course of \( E_c^X([100], \varepsilon) \), \( E_c^X([010], \varepsilon) \) is identical (see Fig. 3).

For the valence band the coupling between light-hole and split-off band results in more complex expressions [45]. With \( \delta E = \frac{1}{4} a_{ab}(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}) \) one obtains:

\[ E^{3H}(\Gamma, \varepsilon) = E^L + a_{tr}(\varepsilon) - \delta E, \]

\[ E^{3H}(\Gamma, \varepsilon) = E^L + a_{tr}(\varepsilon) + \frac{1}{2}(\delta E - \Delta_{SO}) + \frac{1}{2}(\sqrt{\Delta_{SO}^2 + 2\Delta_{SO}\cdot \delta E + 9\delta E^2}) \]

(6)

\[ E^{3H}(\Gamma, \varepsilon) = E^L - \Delta_{SO} + a_{tr}(\varepsilon) + \frac{1}{2}(\delta E + \Delta_{SO}) - \frac{1}{2}(\sqrt{\Delta_{SO}^2 + 2\Delta_{SO}\cdot \delta E + 9\delta E^2}) \]

(7)

with \( a_c \) being the absolute deformation potential and \( a_{ab} \) the uniaxial shear deformation potential in [100]-direction of the valence band. \( \Delta_{SO} \) denotes the spin-orbit splitting and \( E^L \) the energy of the unstrained valence band edge.

Remarkably, there is a large coupling of light-hole- and split-off band (through the term \( 2\Delta_{SO}\cdot \delta E \) under the root of Eq. (6) owing to both a sizable spin-orbit coupling, \( \Delta_{SO} \), and a large biaxial strain leading to large values of \( \delta E \). As result the light-hole band becomes upshifted by at least 100 meV within the QD.

**Piezoelectricity**

Piezoelectricity is defined as the generation of electric polarization by the application of stress to a crystal lacking a center of symmetry [46]. Following our previous work [21, 38, 47] we calculate the piezoelectric charges in first and second [19] order. The resulting piezoelectric potential is obtained by solving Poisson’s equation, taking into account the material dependence of the static dielectric constant \( e_r(r) \).

The relative importance of second order piezoelectricity over its first order components can be judged by evaluation of the ratio \( P_{2nd}^2/P_{1st}^2 \) [21] with \( P_{2nd}^2 = 2B_{124}\varepsilon_{xy}(\varepsilon_{xx} + \varepsilon_{yy}) \) and \( P_{1st}^2 = \varepsilon_{14}\varepsilon_{xy} \) where \( P_z^2 \) is the vertical component piezoelectric polarization, \( \varepsilon_{xx}, \varepsilon_{yy} \) are diagonal strain components induced by the lattice mismatch compensation, and \( \varepsilon_{xy} \) is the \( xy \)-shear strain component. The parameter values of \( B_{124} \) and \( e_{14} \) are taken from Ref. [48]. Note, that since the ratio \( P_{2nd}^2/P_{1st}^2 \) does not depend on \( \varepsilon_{xy} \) the results in Fig. 4 are quite general and do not depend on the specific quantum dot morphology. The larger the lattice mismatch becomes, the more dominant is the magnitude of the second order \( z \)-component: for In-rich QDs, for example, \( P_z^2 \) is more
than seven times larger than \( P_{\text{conf}}^{1st} \) with the corresponding consequences in the context of, e.g., the excitonic FSS. The latter will be discussed further below.

### Coulomb interaction

As soon as more than one charge carrier is confined inside the QD, the influence of direct Coulomb interaction, exchange effects, and correlation lead to the formation of distinct multiparticle states which are calculated using the CI method. This method rests on a basis expansion of the excitonic Hamiltonians into Slater determinants which consist of antisymmetrized products of single-particle wave functions either obtained from eight-band \( k \cdot p \) theory (\( \Gamma \)-point states) or effective-mass theory (\( L \)- or \( X \)-point states). The applied method is applicable within the strong confinement regime as the obtained basis functions are already similar to the weakly correlated many-body states [22, 49–51].

### Optical properties

The interband absorption and emission spectra are calculated by Fermi’s golden rule applied to excitonic states calculated by the CI method. In this paper we focus on \( \Gamma \)-point transitions only and leave the other results for a separate publication. The radiative rates \( R \equiv \Gamma_{if} \) and transition probability \( P_{if} \) of the considered \( \Gamma \)-point transitions are calculated according to

\[
P_{if} = \frac{t}{\hbar} \left( \frac{\epsilon}{m} \right)^2 \frac{2\hbar\omega}{e^2} \left| \epsilon \cdot (i | \nabla | f) \right|^2,
\]

\[
R \equiv \Gamma_{if} = \frac{P_{if}}{t} \quad \text{with}
\]

\[
(i | \nabla | f) = \sum_{j,k} (F_j u_j^F | \nabla | F_k u_k^F)
\]

\[
= \sum_{j,k} \{\delta_{jk} \langle F_j | \nabla | F_k \rangle + \langle F_j | F_k \rangle \langle u_j^F | \nabla | u_k^F \rangle\}
\]

where \( F_j \) denotes the envelope function, \( u_j^F \) the associated Bloch function with band index \( j \), and \( \epsilon \) is the polarization vector.

### CONFINEMENT POTENTIALS

We start with the single-particle confinement potentials \( E_{\text{conf}} \) for electrons and holes and show the results in Fig. 4 for \( E_{\text{conf}} \) along the QD growth axis parallel to [001] crystal direction computed without and with the inclusion of elastic strain. We firstly notice that the strain has considerable effect on \( E_{\text{conf}} \) except for \( X_{[100]/[010]} \) states which are bound inside QD body and for which

![Diagram showing the confinement energy of electrons for several points of \( k \)-space (\( \Gamma \), \( X \), and \( L \)) and of holes at \( \Gamma \), given along [001] crystal direction along QD vertical symmetry axis. We show on the left (right) column \( E_{\text{conf}} \) without (with) considering the strain field in and around a QD. The insets show the designation of bands and the sketch the direction where the evaluation of \( E_{\text{conf}} \) was performed with respect to Fig. 2. Note, that we show only \( X_{[100]/[010]} = 1/2 \times (X_{[100]} + X_{[010]}) \) and \( L_{\text{all}} = 1/4 \times \sum_{i=1}^4 L_{li} \) here, see text. The capital letter A, B, C, and D mark the concentrations listed in Tab. II.

\( E_{\text{conf}} \) attains the lowest energy in our structure, similarly as for \((\text{In,Ga})\text{As/GaP QDs}) \). On the other hand, the bands which are influenced much more by strain are \( X_{[001]} \) and particularly \( \Gamma \) for which the strain can even revert the position of the minimum of \( E_{\text{conf}} \) outside of...
QD body. For the former (X[001]) the minimum of $E_{\text{conf}}$ occurs above QD due to the tensile $\epsilon_{zz}$ strain exerted by the dot body. We note that similar effect occurs also in SiGe/Si and (In,Ga)As/GaP QD systems. For the latter (Γ) the minimum is found in the GaAs-IL for Sb rich dots. As shown in Ref. [25], during the growth an Sb-soaking after the GaAs-IL deposition is employed prior to QD-nucleation. This is very likely to trigger an As-for-Sb anion exchange reaction at the GaAs-IL surface, leading to GaSb formation and thus a considerable material intermixing in the QD layer. Therefore, such intermixing leads there to the minimum of $E_{\text{conf}}$ for Γ-electrons ($E_{\text{c,Γ}}$, $E_{\text{conf,Γ}}$) to be strongly positionally dependent in In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs/GaP QDs. Finally, we note that $E_{\text{conf}}$ for L bands are affected by a mere increase in energy.

RESULTS FOR SINGLE-PARTICLE STATES

![Single-particle eigen energies](image)

![Electron–hole transition energies](image)

**FIG. 5.** (a) Ground state single-particle eigen energy ($E_{\text{sp}}$) and (b) electron-hole transition energy ($E_{\text{eh}}$) for selected alloys as described in Tab. I. For L- and X[100]/[010] electrons the plotted energies are averaged over the first 8 almost degenerate L-levels labelled L all and over the first 4 almost degenerate X-levels, denoted with X[100]/[010]. Interestingly, $E_{\text{sp}}$ for Γ-electron states crosses that for L all close to point C in the middle panel of Fig. 5 (a) and both L all and X[001] close to point D in the rightmost panel of Fig. 5 (a).

However, since $E_{\text{sp}}$ of electrons does not change that much with dot composition, the energies of the transitions between electrons and holes ($E_{\text{eh}}$) are dictated by $E_{\text{sp}}$ of the latter, see Fig. 5 (b). Similarly as for Fig. 8, $E_{\text{sp}}$ of holes is mainly influenced by antimony content which is, indeed, one of the main features of our QD system. The energies of holes, thus, cause the large increase in $E_{\text{eh}}$ of ∼500 meV for recombinations between Γ-electron to Γ-hole states or even up to ∼700 meV for transitions from X[100]/[010], see middle panel of Fig. 5 (b). On the other hand, $E_{\text{sp}}$ of electrons dictates the energy ordering of $E_{\text{eh}}$ which is for most Ga and As concentrations from highest to lowest: Γ, L all, X[001], and X[100]/[010], see Fig. 5 (b). This is also the case for the energy flipping of $E_{\text{eh}}$ for transitions from Γ and L all or X[001] to Γ holes.

We now proceed with the results for single-particle states of our In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs/GaP QDs. For the alloys listed in Tab. I we show the results for electron and hole ground state energies ($E_{\text{sp}}$; Γ-, L-, and X-electron and Γ-hole) and the related inter-band transition energies in Fig. 5. First of all we observe that the first eight states involving L-electrons are almost degenerate in energy, hence, we do not distinguish between them in Fig. 5 and group them under the label L all. The same holds true for (X[100], X[010]) electrons, which we denote X[100]/[010].
FIG. 6. Side and top views of the probability densities of electrons [el] and holes [hl] in \( \text{In}_{1-x} \text{Ga}_x \text{As}_y \text{Sb}_{1-y} / \text{GaAs} / \text{GaP} \) QDs (grey objects). Cuts through the plane parallel (perpendicular) to the QD symmetry axis are given from the first to the fourth (fifth to eighth) column for Ga and As contents denoted by A, B, C, and D in Tab. I. The designation of the quasi-particles and the corresponding Bloch waves is given in the ninth column. The properties of QD is the same as that in Fig. 2 (c). The single-particle electron and hole envelope functions for \( \Gamma \)-point Bloch states are calculated using 8x8kp (see main text), those for \( X \)- and \( L \)-electron states by 1x8kp. The isosurfaces encircle 90% of total probability density. Due to the \( k \)-space (a)symmetry, some of the \( X \) and \( L \) states for QD with circular base are degenerate in (001) plane, thus, we group them together in the lower three rows of the figure. In the top row of the figure we show the crystallographic orientations to facilitate the comparison with the orientation of the probability densities.

We proceed with the inspection of wavefunctions of \( \text{In}_{1-x} \text{Ga}_x \text{As}_y \text{Sb}_{1-y} / \text{GaAs} / \text{GaP} \) QDs for Ga and As contents A, B, C, and D (see Tab. I), and we show that in Fig. 6. We find that the spatial location of the probability densities of states confirms our expectations drawn from the inspection of \( E_{\text{conf}} \) in Fig. 4. In particular, it allows us to make an assignment of the type of confinement of the \( \Gamma \)-electrons in real space. Hence, C and D contents seem to correspond to type-I transition of \( \Gamma \)-electrons to \( \Gamma \)-holes, while B content is type-II, and A corresponds to the transition between those two types of confinement. Further, the spatial position of wavefunctions indeed confirms that transitions involving \( X_{[001]} \)-electrons are of type-II, and those for \( L_{[110]}/[1\bar{1}0] \) of type-I nature in real space regardless of Ga and As contents in the dot.

However, the assignment of \( \Gamma \)-transitions can be done more precisely based on the inspection of the corresponding electron-hole (\( -J_{\text{eh}} \)) Coulomb integral, see Fig. 7. We see that \( -J_{\text{eh}} \) is by far smaller for type II compared to type I owing to the spatial separation of the quasiparticles. Clearly, type I occurs in our system for dots rich in Indium and Arsenic, while those with larger Ga and Sb tend to be type-II. Notice also the comparison between GaP and GaAs substrates in Fig. 7. We will return to the identification of the type of confinement from the properties of excitons in the following.

Now, however, we would like to point out that the separation of \( \Gamma \)-electron wavefunctions that are type-II in real space for \( x = 0.8, y = 0.2 \) into two segments, seen in Fig. 6, is qualitatively similar to that occurring.
for hole states in type-II (In,Ga)As QDs overgrown with GaAs(Sb) layer [52]. However, in the present system the segments of Γ-electrons are oriented along [110] direction as opposed to [110] for (In,Ga)As/GaAs(Sb)/GaAs QDs. Noticeably, electron wavefunctions form molecular-like states [53] as discussed in Ref. [74] as well. Due to low coupling of the spins of electrons to that of the atomic nucleus, the In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs/GaP QD system provides potentially much lower dephasing [53] than the (In,Ga)As/GaAs(Sb)/GaAs QDs studied in Ref. [54].

Hole localization energies and storage time

![Diagram of Hole binding energy for GaP, GaAs, and GaAs substrate](image_url)

FIG. 8. Binding energies of single-particle hole states ($E_{b,H}$) for In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$ QD with GaAs IL grown on GaP (left column) or on GaAs (right column) substrates. The single-particle hole energies $E_{b,H}$ necessary for the computation of $E_{b,H}$ (see text) were obtained within the envelope approximation based on $\mathbf{k} \cdot \mathbf{p}$ method. Notice that dots grown on GaP provide more than twice larger $E_{b,H}$ than those on GaAs. Except for the composition, the QD structural properties were the same as those in Fig. 2 (c). The capital letter A, B, C, and D mark the concentrations listed in Tab. I. For the alloy interpolation scheme see Eqs. (1a) and (1b).

The variations of the QD valence band edge energies upon chemical composition translates into a large variation of the hole localization energy defined by $E_{b,H} = E_H - E_{\infty,\Gamma}^v$, with $E_H$ being the energy of the single-particle hole state and $E_{\infty,\Gamma}^v$ the substrate material Γ valence band energy, respectively. The results for the localization energy $E_{b,H}$ are shown in Fig. 3 as function of the alloy parameters $x$ and $y$ in In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$ QDs on GaAs-IL grown either on GaP or GaAs substrates. Evidently, the QDs grown on GaP exhibit more than twice the localization energy $E_{b,H}$ compared to QDs on GaAs, thus, confirming the importance of substrate material for QD-Flash concept [25].

The energy $E_{b,H}$ can be translated into the storage time of QD-Flash memory units by using the expression

$$\tau = \frac{1}{\gamma \sigma_{\infty} k_B T^2} \exp \left( \frac{E_{b,H}}{k_B T} \right),$$

with $\gamma = \sqrt{3(2\pi)^3} E_H m_0^* k_B^2 / h^3$ depending on the bulk material valence Γ-band effective mass $m_0^*$, $k_B$ being the Boltzmann constant, $\sigma_{\infty}$ the capture cross-section, and $T$ the temperature. If we let $m_0^*$ depend on the alloy parameter $x$ and $y$ and choose $\sigma_{\infty} = 9 \times 10^{11} \text{ cm}^2 \text{s}^{-1}$ from Ref. [26] we find that the maximum $E_{b,H} = 1.32 \text{ eV}$ in Fig. 3 relates to a storage time of 5000 s, occurring for pure GaSb QD with GaAs-IL grown in GaP.

The carrier cross-section is a sensible parameter entering the calculation of the storage-time: it depends on the chemical composition and the QD-morphology itself (cmp. Ref. [57]: $\sigma_{\infty} = (8 \pm 5) \times 10^{10} \text{ cm}^2$ and Ref. [26]: $\sigma_{\infty} = (9 \pm 5) \times 10^{11} \text{ cm}^2$). Both properties are subject of constant technological optimization. The value of the carrier cross-section is not part of our modelling scheme but enters the calculation as external parameter.

Γ-EXCITONS

We utilize the obtained single-particle wavefunctions as basis states for CI calculations and compute the corresponding exciton ($X^0$) states. Since we previously set $P_{k\neq 0} = 0$ it is reasonable to evaluate in the following $X^0$ consisting of Γ-electrons and Γ-holes only ($\Gamma-X^0$) to avoid omission of some Coulomb elements for complexes involving $k \neq 0$ electrons.

We first discuss the emission radiative rate ($R$) of $X^0$ calculated using the Fermi’s Golden rule, see Ref. [22] for details. The results for a variety of Ga and As contents are shown in Fig. 4 and together with Fig. 7 allow us to find the contents for which In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$ QDs on GaAs IL in GaP show type-I or type-II confinement. Type I can be expected for $x + y \gtrsim 1$ and consequently type II for $x + y \lesssim 1$. We also show in Fig. 4 the values of $R$ for the same dots on GaAs substrate for comparison. As expected, type II is associated with the amount of GaSb intermixing in the QD structure as found also elsewhere [52]. Interestingly, type I for GaAs substrate occurs mostly for QDs with larger amounts of As than for GaP substrate. Along with larger $D$ for dots with larger In content this a result of much increased hydrostatic strain due to GaP substrate providing considerably larger confinement for quasiparticles. The aforementioned hints to the conclusion that QD structures grown on GaP might perform even better in optoelectronic applications than those grown on GaAs substrates which are currently under study [58].

We now proceed with the fine structure of $X^0$. That is caused in (In,Ga)As/GaAs QDs [23] [77] [78] by the effects of isotropic ($J_{\text{iso}}^{\text{exch}}$) and anisotropic ($J_{\text{aniso}}^{\text{exch}}$) exchange
interaction which is the case also for the present system. The former causes the energy separation of bright and dark $X^0 (\Delta E_{bd})$ while the latter results in FSS.

The results for our dots are shown in Fig. 10 again for both GaP and GaAs substrates. We find FSS of $X^0$, to be in the range of $\sim 180 - 300 \mu eV$ and $\Delta E_{bd}$ of $\sim 400 - 600 \mu eV$ for both substrates in type-I regime. On the other hand, for type II those parameters drop to values $\lesssim 100 \mu eV$. We note that the calculations of FSS and $\Delta E_{bd}$ involved expansion of the exchange interaction into multipole series [23, 24]. Following Ref. 59 we considered the following terms of that expansion: monopole-monopole (EX$_0$), monopole-dipole (EX$_1$), and dipole-dipole (EX$_2$). We find that irrespective of the substrate material (GaP or GaAs) the FSS in our system is dominated by EX$_2$. On the other hand, EX$_0$ and EX$_1$ contribute to FSS and $\Delta E_{bd}$ of only $3 - 10 \mu eV (\lesssim 0.5 \mu eV)$ and $\sim 30 \mu eV (\lesssim 1 \mu eV)$, respectively, for type-I (type-II) confinement. We further note that considerably smaller FSS for type-II corroboration with the results of Refs. 59, 61 for (In,Ga)As/Ga(As,Sb)/GaAs QDs and, in turn, confirms that to be a rather general property of dots which are type-II in real space.

The correlation is obtained in our CI calculations through admixing of excited single-particle states [22]. By taking the basis of two (six) ground state electron and two (six) hole states for calculations without (with) the effects of correlation we have found the effect on FSS and $\Delta E_{bd}$ energies to be $\sim 2 \mu eV$ (not shown). In total, the above findings make In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$ QDs with GaAs IL on GaP substrate a promising candidate for realization of quite optically bright single photon sources, different to type-I (In,Ga)As/GaAs QDs which are currently being under investigation as sources of light for quantum cryptography applications [58, 62, 63].

Finally, we would like to provide a useful way of experimental determination the type of confinement in In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs/GaP QDs based on measurement of the polarization of emission of $\Gamma$-$X^0$, motivated by Ref. 61. For the incoherent sum of the bright $X^0$ doublet we show in Fig. 11 the polarization azimuth and the degree of linear polarization (DOLP), defined by

$$DOLP = \frac{R_{\max} - R_{\min}}{R_{\max} + R_{\min}},$$

where $R_{\max}$ and $R_{\min}$ denote the maximum and minimum $R$, respectively. Note that the azimuth is given in terms of the crystallographic axes in order to ease the comparison with the shape of the wavefunctions, shown in Fig. 6. Similarly as in Ref. 61, we find that the azimuth of $X^0$ in type-II regime follows the orientation of
the elongation of the wavefunction of the quasiparticle which is outside of the dot body. As discussed also earlier, contrary to Ref. [61] in the present system the quasiparticles outside of QD are electrons which are elongated along [110] axis, hence, the orientation of the azimuth in type II. In type I, on the other hand, the azimuth is dictated by the anisotropy of hole wavefunctions which is along [100] axis. Thus, the 90° flip of the polarization azimuth of emission from In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs/GaP QDs when going from transition from type I to type II is a clear sign of the type of confinement.

On the other hand, DOLP of the incoherently summed $\Gamma$-$X^0$ is close to zero in type-I In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs IL irrespective of the substrate. However, that is approaching ~ 0.5 for type II in case of QDs grown on GaP substrate but not on GaAs. This is a consequence of the GaAs IL under QDs providing additional confinement for $\Gamma$-electrons which is not present, however, for In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs IL.

We finally note that the values of FSS, bright-dark energy separation and DOLP might be slightly different in dots which do not have uniform alloy content or are elongated.

**CONCLUSIONS**

Studies of the electronic structure of In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs quantum dots grown either on GaP or GaAs substrates were presented. We first determined the confinement potentials for $k \neq 0$ and $k = 0$ conduction and $k = 0$ valence bands. The latter along with the calculated single-particle hole states enabled us to determine the most promising candidate structures for the realization of the QD-Flash memory concept from this system. Based on the calculated confinement potentials we proceeded with the determination of single-particle electron and hole states and the energy ordering of their mutual transitions. Here we thoroughly discussed the method of $k \cdot p$ calculations for $k$-indirect transitions and determined the form of the momentum matrix element that needs to be determined for such calculations to be correct. For transitions between $\Gamma$-electron and $\Gamma$-hole states we computed also the excitonic states. Investigating their emission rates we identified for which concentrations of dot material constituents type-I or type-II confinement should be expected and we have shown FSS and bright-dark splitting including the effect of the multipole expansion of exchange interaction. Moreover, we have provided a neat method to experimentally determine the type of confinement from the measurements of the polarization of photoluminescence.

In conclusion, using direct comparison with the (In,Ga)As/GaAs system we have shown that In$_{1-x}$Ga$_x$As$_y$Sb$_{1-y}$/GaAs/GaP quantum dots are probably more useful for effective realization of most of the building blocks for quantum information technology based on quantum dots, like entangled-photon sources or qubits.

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