Tailoring the emission wavelength and s-p splitting in MOCVD-grown InGaAs/GaAs quantum dots emitting above 1.3 μm

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The electronic structure of strain-engineered In0.75Ga0.25As/GaAs quantum dots emitting in the telecommunication O band is probed experimentally by photoluminescence excitation spectroscopy on the single-dot level. The observed resonances are attributed to p-shell states of individual quantum dots. The determined energy difference between s- and p-shells shows an inverse dependence on the emission energy. This observation is attributed to the varying indium content within individual quantum dots, indicating a way to control the quantum dot electronic structure. The impact of the size and indium content in the investigated quantum dots is simulated with an 8-band k·p model supporting the interpretation of the experimental data.

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Security of data transmission has become an important issue in information technology. Most of the information nowadays is stored and exchanged digitally, with a majority of the transfers being secured by public-key cryptography. However, the development of quantum computing has shown disturbingly easy ways to overcome classical cryptography security, which is based on the assumption of limited computer performance. Particularly, the Shor's algorithm has demonstrated that the number factorisation (and thus the decryption) can be performed in computation time shorter by a polynomial factor.1) This has led to the intensification of research focusing on truly secure communication – quantum cryptography.2) For the practical realisation of device-independent quantum key distribution or long-distance quantum communication via optical fibres, single-photon sources operating at telecommunication wavelengths are key building blocks.3)

One of the most promising systems for the realisation of single-photon sources based on truly quantum emitters are semiconductor quantum dots (QDs),4) which have been shown to work well at the telecommunication wavelengths, e.g. in the low dispersion O band.5–7) Moreover, for this spectral range there has been already demonstrated optical-fibre-compatible single-photon emission based on quantum dots.8–10) Further optimisation is still necessary to increase (in a controlled way) the collection efficiency by, e.g., decreasing the QD surface density and deterministically integrate QDs into optical cavities or other photonic structures increasing the extraction of the emitted photons.11) To obtain efficient emission in the telecom O band there can be used InGaAs QDs on GaAs substrate (typically emitting around 1 µm) with an additional InGaAs strain-reducing layer (SRL) resulting from the InGaAs-GaAs lattice constants mismatch and shifting the emission to the desired 1.3 µm.12–16) The incorporation of an additional layer in the vicinity of QDs during the growth process influences the local strain and therefore their size and composition as well as the depth of the confining potential, modifying the electronic structure expected for typical and well-established InGaAs/GaAs QDs (i.e., without additional layers). Therefore, to fully understand and use this kind of emitters as quantum light sources it is essential to learn about their electronic structure. In particular, the highest purity of single-photon emission has been obtained using p-shell excitation scheme17) and it requires precise knowledge of the confined exciton excited states spectrum of individual QDs including the p-shell state energies. Moreover, for the design of these kind of sources it would be beneficial to have the possibility to tailor both, the QD ground state energy (i.e. emission wavelength) and the energetic distance from the ground state to the excited state, preferably separated by at least the thermal energy (e.g. 25 meV at room temperature) from the emitting quantum dot ground
state to provide good thermal stability and spectral isolation. Therefore, it is crucial to identify determinants and propose means to control the electronic structure of these application-relevant epitaxial nanostructures, especially important for nanophotonic applications, like efficient sources of single or entangled photons at the telecommunication wavelengths compatible with the existing fibre networks. So far, there has been no study on the independent control of emission wavelength and energy separation between ground and excited states in single O-band-emitting InGaAs/GaAs quantum dots with strain-reducing layer.

In this report we determine the energetic splitting between p-shell and s-shell states (s-p splitting) in single In$_{0.75}$Ga$_{0.25}$As/GaAs QDs emitting in O band, and show how the s-p splitting can be influenced by the QD composition and size or the In content in the SRL. The investigated sample was grown by metalorganic chemical vapour deposition (MOCVD) on a GaAs substrate with 23 pairs of GaAs/Al$_{0.9}$Ga$_{0.1}$As layers composing a distributed Bragg reflector (DBR), providing increased emission collection efficiency from the following layer of QDs. In$_{0.75}$Ga$_{0.25}$As quantum dots were formed during the Stranski-Krastanov self-assembled growth succeeded by capping with 4 nm of In$_{0.2}$Ga$_{0.8}$As, creating a strain-reducing layer, resulting in indium concentration and QD size favouring 1.3 µm emission. The structure was covered with a GaAs layer (630 nm), from which there was formed an array of microlenses (with no specific QDs preselection) by means of 3D electron-beam lithography. This process also removed QDs outside lenses, leaving areas of QDs with a base diameter of 3.6 µm (the diameter of one lens). The surface density of these QDs was of the order of $10^9$ cm$^{-2}$ with their base diameter of 30 nm, and an average height of 6-8 nm. There was also used a reference sample with an ensemble of similar QDs with slightly different indium composition and with no DBR below the dot layer to prevent overlapping of the DBR characteristics with the spectrally broad emission of a QD ensemble. For the identification of excited state in these quantum dots there was used single-dot photoluminescence excitation (PLE) spectroscopy adapted to the spectral range above 1 µm. QDs were excited by a self-made continuous wave external-cavity tunable laser followed by a short-focal-length monochromator and shortpass filters to provide a clean excitation laser line. For the nonresonant excitation a 639 nm semiconductor laser was used. The QD sample was mounted in a continuous-flow microscopy cryostat providing temperatures down to 5 K. To excite single quantum dots and to collect their emission an achromatic objective with 0.4 numerical aperture was applied, offering a laser spot diameter on the sample surface of single micrometres, which was small enough to excite a single microlens. QD emission spectrum
was detected by a nitrogen-cooled linear array InGaAs sensor coupled to the monochromator.

A typical photoluminescence spectrum for the reference sample with the whole ensemble of InGaAs QDs is presented in Fig. 1(a). It shows the spectral range of quantum dots emission for nonresonant excitation (639 nm; 1.940 eV). There are observed two maxima related to the radiative recombination in QDs. The left one corresponds to the QD ground state (s-shell) emission, while the presence of the second one is a result of a state-filling effect and it comes from the recombination in a higher (p-shell) QD state. The reference sample with an ensemble of this kind of QDs has been studied in detail in Ref. 19. The energy difference between the QD maxima is approximately 70 meV, indicating the expected splitting energy between p-shell and s-shell exciton states within a single In$_{0.75}$Ga$_{0.25}$As QD. This value is relatively high as compared to conventional InGaAs QDs emitting below 1 µm,$^{17,20}$ and should provide good thermal stability of the ground state emission. On the high energy slope of the second maximum there can be noticed a fingerprint of even higher quantum dot state, separated by approx. 130 meV from the ground state – confirming a rather deep confining potential. Figure 1(b) presents an exemplary photoluminescence spectrum on a single-dot level for quasi-resonant excitation (1242 nm; 0.998 eV; i.e. into the expected p-shell state), with a few sharp emission lines observed in the O band spectral range.

An example of a PLE map from single In$_{0.75}$Ga$_{0.25}$As QDs is presented in Fig. 2(a). It shows an evolution of the emission lines from Fig. 1(b) as the excitation energy is tuned in the range of the expected p-shell state energies. Indeed, at some excitation energy values a few of the lines exhibit an enhancement of the emission intensity, suggesting an increase of absorption due to excitation energy coincidence with a higher energy state within a QD. Figure 2(b) shows single-dot PLE spectra, extracted from the map in Fig. 2(a), for two QD emission lines: 1336.9 nm (red) and 1342.5 nm (violet). The maximum in the red PLE spectrum appears 70 meV above the emission energy and the peak in the violet PLE spectrum is located at the energy difference of 74.5 meV. Both these values correspond well with the energy difference between the excited and ground quantum dot states expected from the measurements on an ensemble of similar QDs.$^{19}$ The linewidths of the PLE maxima are relatively broad (~2 meV), which may be related to the relatively large excitation laser linewidth (~0.7 meV)$^{18}$ or can result from a complex energy structure (i.e. dense ladder of states) of the QD excited states.$^{19}$ The energy difference of the observed PLE resonances (preliminarily identified as related to the p-shell absorption) changes with the energy of the emission line. The energy difference between PLE maxima and the ground state emission
(described provisionally as “s-p splitting”) of many studied single In$_{0.75}$Ga$_{0.25}$As QDs is presented in Fig. 3(a) as a function of the QD ground state energy. There is a clear dependence observable: QDs emitting at higher energies exhibit a significant decrease of the “s-p splitting” energy (from 80 down to 60 meV). Both energies should be indeed related, but the expected dependence is usually opposite. This is related to the fact that the ground state energy difference in self-assembled QDs is usually a direct result of the size distribution of QDs within an ensemble. The smaller the dot the higher its ground state energy. However, a decrease of the QD size should at the same time increase the s-p splitting due to stronger energy levels quantization – this is opposite to the behaviour observed for the investigated In$_{0.75}$Ga$_{0.25}$As QDs in this work. The s-p splitting mainly depends on the overall shell energy structure of a QD and less on the effects related to Coulomb interactions and various carrier combinations (excitonic complexes) confined within a QD. The influence of Coulomb interactions on the s-p splitting is typically one order of magnitude weaker (up to a few milielectronvolts), thus the exact character of excitonic complexes related to individual emission lines is of less importance in this study.

To confirm the identification of the observed PLE resonances as the p-shell absorption and to explain the s-p splitting dependence, a single In$_{0.75}$Ga$_{0.25}$As quantum dot energy structure was modelled and its evolution with QD size and material composition was evaluated. The strain distribution in the system was calculated within a continuous elasticity approach$^{21}$ with piezoelectric field based on strain-induced polarization up to the second order$^{22}$. There was also included gradient of indium distribution inside a QD as suggested by structural data (not shown here) where indium was concentrated in the centre of a QD. Single-particle electron and hole states were calculated within the 8-band k·p model$^{23}$ with excitonic states obtained within a configuration interaction approach. More details of the calculations and material parameters are described in Ref. 24. For realistic QD parameters (e.g., diameter of 30 nm, height of 6 nm) the calculated s-p splitting energy is approximately 75 meV, corresponding well to the measured PLE resonances in the range of 60 to 80 meV, thus confirming the identification of the observed experimental maxima. Next, the influence of the QD size on the s-p splitting energy was simulated and the result is shown in Fig. 3(b) – the QD size is changed relatively to the abovementioned dimensions with the size multiplier indicated in the figure (all QD dimensions are changed simultaneously). As expected, the decrease in QD size shifts the ground state energy to higher values and increases the s-p splitting. However, this is in contrary to the experimentally observed dependence. The other parameter expected to alter the electronic structure in In$_{0.75}$Ga$_{0.25}$As QDs, is the indium
content. Its influence on the s-p splitting energy was calculated for strain-reducing layer and QDs, independently, and is also presented in Fig. 3(b). This result shows the same trend as observed in the experiment – a higher ground state energy is associated with lower s-p splitting values. Thus, the dominant factor responsible for s- and p-shell separation in In$_{0.75}$Ga$_{0.25}$As QDs covered by a SRL is not their size but the indium content. The increase of the average indium content (i.e. InAs amount within the InGaAs alloy) leads to lower ground state energy but at the same time effective mass is reduced, resulting in the larger separation between s- and p-shell states. It is important to note that the change of the indium content influences also the lattice mismatch between InGaAs and GaAs and the resulting strain field has an impact on a QD energy structure – this effect was taken into account in the calculations. In the investigated QDs all the simulated parameters (i.e. QD size; QD composition; SRL composition) do change within the ensemble simultaneously, therefore, the absolute energy values from the simulations do not correspond to the experimental s-p splitting values precisely, but support (or not) the observed trends.

In previous studies there was found that a higher indium content in InGaAs/GaAs quantum dots is linked to smaller QDs, however those structures were grown by molecular beam epitaxy and were emitting below 1 µm, so this tendency does not have to be easy transferable to other QDs in the same material system.\textsuperscript{25} The opposite influence of QD size and composition on the s-p splitting (relative to the QD ground state energy) in the investigated structures, demonstrates the possibility of mutual tuning of QD ground and excited states energies, offering an additional degree of freedom in novel quantum nanodevices engineering. Furthermore, when looking at the calculated s-p splitting for electron and hole single particle states, it is shared 35:65 between the valence and conduction bands, respectively, corresponding to approximately 21-28 meV for holes and 39-52 meV for electrons (depending on the specific QD), providing the energetic separation large enough to prevent any significant thermal escape of charge carriers from ground to higher QD states, increasing the overall thermal stability of devices based on In$_{0.75}$Ga$_{0.25}$As QDs.

In summary, we have studied In$_{0.75}$Ga$_{0.25}$As/GaAs quantum dots capped with a strain-reducing layer providing QD emission redshift to the telecom O band. Single QD photoluminescence excitation spectroscopy has allowed for the determination of the energy splitting between s- and p-shell in individual QDs, revealing a reduced splitting for dots emitting at higher energies. Supported by theoretical modelling, this behaviour has been associated with a varying indium content in different QDs within the ensemble. The ability
to influence both, the ground state emission (by the size of a quantum dot) and the s-p splitting energy (by altering the indium content) provides an additional degree of freedom in the design and growth of QDs for O band spectral range applications, like telecom single-photon sources with p-shell quasi-resonant pumping.\textsuperscript{9} In particular, it allows to obtain better spectral isolation of the ground state transition, increasing the activation energy for carrier escape via higher energy states in a quantum dot and providing high temperature stability. The investigated structures had been grown by MOCVD, which is also of practical importance, since this technology offers lower production costs and hence is better suited for large-scale device fabrication than molecular beam epitaxy.

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Figure Captions

**Fig. 1.** (a) Photoluminescence spectrum from a reference sample with an ensemble of InGaAs/GaAs QDs obtained under non-resonant excitation conditions (639 nm; 1.940 eV) with estimated energy differences between consecutive QD states. (b) Single QD photoluminescence spectrum for quasi-resonant excitation (1242 nm; 0.998 eV) of InGaAs/GaAs QDs. Both spectra were recorded at 5 K.

**Fig. 2.** (a) Single QD photoluminescence excitation map in the spectral region of excited states in InGaAs/GaAs QDs. (b) Single QD photoluminescence excitation spectra for two emission lines from the map (red: 1336.9 nm, violet: 1342.5 nm). The measurements were performed at 5 K.

**Fig. 3.** (a) InGaAs/GaAs QDs s-p splitting energies, derived from photoluminescence excitation measurements on many single QDs, as a function of their ground state energy. (b) 8-band k·p simulations of InGaAs/GaAs QD for varying QD size (expressed by a size multiplier as described in the text) and indium composition in the QD and SRL. The resulting s-p splitting is displayed as a function of the QD ground state energy.
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