We perform experimental and theoretical studies of the electronic structure and relaxation processes in pyramid shaped InAs/GaAs quantum dots (QDs), grown by molecular beam epitaxy in the Stranski–Krastanow growth mode. Structural properties are characterized with plan view and cross section transmission electron microscopy.

Finite difference calculations of the strain and the 3D Schrödinger equation, taking into account piezoelectric and excitonic effects, agree with experimental results on transition energies of ground and excited states, revealed in luminescence and absorption spectra. We find as relative standard deviation of the size fluctuation $\xi = 0.04$; the pyramid shape fluctuates between $R_1=101$ and $R_2=203$ side facets.

Carrier capture into the QD ground state after carrier excitation above barrier is a very efficient process. No luminescence from excited states is observed at low excitation density. Energy relaxation processes in the zero-dimensional energy states are found to be dominated by phonon energy selection rules. However, multi-phonon emission (involving GaAs barrier, InAs wetting layer, InAs QD and interface modes) allows for a large variety of relaxation channels and thus a phonon bottleneck effect does not exist here.

1. Introduction

The fabrication of quantum dot arrays with heteroepitaxy in the coherent islands Stranski–Krastanow growth regime [1–11] seems to be one of the most promising approaches to reach one of the ultimate goals of nanostructure research: the quantum dot (QD) laser with its predicted temperature independent low threshold current density [12,13]. This unique property is due to the $\delta$-function like density of electronic states in each QD which was demonstrated experimentally [9,14]. Recently, the first lasers based on such nm-scale, self-organized quantum dots were reported [15,16].

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Detailed understanding and tailoring of properties and performance of quantum dot based optical devices requires theoretical modelling of their electronic states. In the case of strained islands, simulation of the three-dimensional strain distribution and subsequent solution of the 3D Schrödinger equation in the modified confinement potential is necessary and has been first performed in Grundmann et al. [17]. In this paper we will investigate the influence of size and shape on the electronic states in InAs/GaAs quantum pyramids. The theoretical results will be compared with experimental luminescence spectra.

Equally important as the electronic structure of the quantum dot are the carrier capture and energy relaxation processes. Generally, capture and relaxation into the QD ground state from above barrier excitation seem to be very efficient since the quantum efficiency of QD luminescence is comparable to best quantum well samples and at low excitation density no other than QD ground state luminescence is present. Only at higher excitation densities, when the ground state saturates, excited levels appear. At first surprisingly, however, the revelation of excited electronic states with photoluminescence excitation spectroscopy fails in the sense that the spectrum is dominated by peaks at multiple LO phonon energies rather than by excited electronic states [6,18]. Such experiments thus allow to study the energy relaxation in the QDs.

The paper is organized as follows: after a brief description of our experimental methods (Section 2), we discuss the strain distribution in and around the InAs pyramids (Section 3). In addition the driving mechanism for vertical ordering of QDs is discussed. In Section 4 we present the electronic structure of the quantum pyramids as a function of size and shape. In the light of the theoretical simulation we interpret luminescence data obtained from arrays of such QDs (Section 5). In Section 6 we describe PL excitation experiments and discuss the applicability of the ‘phonon bottleneck’ effect.

2. Experimental

Our samples are grown by molecular beam epitaxy on GaAs (001) substrates. Details about the growth procedure can be found in Grundmann et al. [9]. For an average deposited InAs thickness $t_{av}$ above 1.6 monolayers (ML), the InAs layer transforms into coherent islands. For 4 ML deposition...
we obtain dense arrays (about 10^{11} \text{ cm}^{-2}) of equilibrium size quantum pyramids with a typical base length of L_b = 12 nm. The base sides are oriented along [100] and [010] interface directions, the side facets are close to \{101\} and \{203\} [9,11] (Fig. 1). In dense arrays, when island–island interaction via the substrate is significant, the dots arrange into a square lattice, distorted by statistical fluctuations [9,11]. Our numerical calculations show that this arrangement is energetically more favorable than rectangular, checkerboard or hexagonal arrays for the same area coverage. More dilute arrays, but with the same pyramid size, are obtained for only 2 ML deposition and growth interruption [19].

Transmission electron microscopy (TEM) studies are carried out in a high voltage JEOL JEM1000 microscope operated at 1 MV. Photoluminescence (PL) is excited using the 632.8 nm line of a He–Ne laser and detected using a cooled Ge photodetector. PL excitation spectroscopy is performed with tungsten halogen lamp dispersed by a 0.35 m double grating monochromator as tunable light source and detected with a 0.75 m double grating monochromator and a cooled Ge photodiode. Calorimetric absorption spectroscopy (CAS) is carried out at T = 500 mK. Minimal detectable zd products are as low as 10^{-5} [20]. Our numerical calculations (typically solving for 10^{6} variables) are performed on a DEC Alpha AXP 3000/600 workstation with 128 MByte RAM.

3. Strain distribution

Figure 2 depicts the QD geometry we will use subsequently. First we discuss pyramids with \{101\} facets, while later on also \{203\} facets are considered. Before we start our discussion, we like to emphasize that the following does only apply to QDs surrounded by barrier material. In the case of uncovered QDs just after deposition, surface contributions to the total energy are essential in particular to explain self-ordering of size and shape [16,21].
The strain distribution around a 3D confined object depends only on its shape but not on its size [17,22]. The strain distribution \( \varepsilon \) scales linearly with the lattice mismatch \( \varepsilon_0 \), \( \varepsilon \propto \varepsilon_0 \). The strain generally decays with the third power of the distance. Analytical solutions can be obtained for a sphere of isotropic material [17]. For realistic QD geometries we use a numerical approach, employing a finite difference method [17]. An important point is that for a strained layer quantum well the barrier is unstrained and the strain distribution [23] does not depend on the elastic properties of the barrier. The amount of strain relaxation of a quantum dot depends on the stiffness of the barrier, thus making it dependent on both the QD and barrier elastic constants. The isotropic (hydrostatic) part of the strain is mainly inside the QD, while the biaxial and shear components are shared between inner and outer material, as expected from a simple analytical model [17].

Figure 3 shows the strain distribution in the wetting layer and along the lines A and B of Fig. 2. The solid line in Fig. 3 denotes \( \varepsilon_{zz} \), the dashed line \( \varepsilon_{xx} \) and the dotted-dashed line \( \varepsilon_{yy} \). Figure 3A shows the linescan intersecting the wetting layer far from the dot is. In Fig. 3B the intersection goes through the top of the pyramid (line A in Fig. 2). In both cases symmetry imposes \( \varepsilon_{xx} = \varepsilon_{yy} \). In Fig. 3C the linescan intersects the dot at one half of the base length in [100] direction from the center (line B in Fig. 2). In the wetting layer (Fig. 3A) the strain is biaxial and entirely confined to InAs. The wetting layer is affected by the QD only in its vicinity, within a distance of about half of the pyramid’s base length.
The linescan through the center of the QD (Fig. 3B) reveals a very different situation. Close to the lower interfaces, \( \varepsilon_{zz} \) is still positive but much smaller (\( \approx 3\% \)) than in the wetting layer because the substrate can no longer force the interface lattice constant to be that of GaAs. With increasing height within the dot \( \varepsilon_{zz} \) changes its sign and becomes negative at the top of the pyramid. This happens because at the very top only little forces act on the QD in the xy-plane, but the GaAs barrier compresses the pyramid mainly from the sides along the z-direction, imposing tensile strain components in the xy-plane (\( \varepsilon_{xx} = \varepsilon_{yy} \) at the top becomes positive). We emphasize that generally, however, the strain is still compressive, even at the top of the pyramid (Trace \( \varepsilon < 0 \)). Around the pyramid also the barrier becomes significantly strained (\( \approx 3\% \) close to the interfaces).

Directly above the InAs pyramid the GaAs is under tensile in-plane strain, while in between dots the strain is compressive. This is driving the vertical ordering of multiple QD layers [1,24]. Figure 4A shows the decay of the tensile in-plane strain \( \varepsilon_{xx} + \varepsilon_{yy} \) (the relative change of surface unit cell area) at the surface above a 12 nm base length InAs pyramid with \{101\} facets for different distances of the surface from the top of the pyramid. Even for quite large barrier thickness of 10 nm a strain in the \( 10^{-3} \) range is still present. Figure 4B depicts the (almost radially symmetric) strain distribution \( \varepsilon_{xx} + \varepsilon_{yy} \) on a surface 5 nm above the pyramid. InAs deposited on top of such an inhomogeneously strained surface [1,24] finds directly on top of the pyramid the largest substrate lattice constant and thus the most favorable energetic conditions.

4. Electronic states

The strain distribution modifies the confinement potential which enters the effective mass Schrödinger equation. From the strain we calculate the local modification of bulk bandgaps as described in Grundmann et al. [17]. The electron experiences the hydrostatic bandgap shift. For the holes we diagonalize the \( 6 \times 6 \) Hamiltonian [25,26], thus taking into account corrections due to the split-off band. Only heavy holes play a role for the localized states since the biaxial strain strongly pushes light holes away from the valence band edge. The heterostructure band offsets are taken from model-solid theory [27]. The influence of the superlattices underneath and above the pyramid has been modeled. It can though be neglected since it affects the electronic levels by less than 1 meV for the given geometry.

An additional effect has to be included at this stage. The shear strains give rise to a piezoelectric polarization which results in non-vanishing local charges at the \{112\}-like edges of the \{101\}
Fig. 5. Wavefunctions for electrons and holes in a 12 nm InAs/GaAs quantum pyramid with (A) \{101\} and (B) \{203\} side facets. Orbitals are given for 70% probability. Hole wavefunctions are indexed according to nodes in the different directions. In (C) the electron wavefunctions for a 7 nm and a 12 nm base side \{101\} facet pyramid are compared. In (D) the same comparison is given for the hole ground state.
pyramid facets [17]. Neighboring edges have opposite charges. The resulting piezoelectric potential \( V_p \) [28], which has to be added to the confinement potential, has thus no 90° rotational symmetry around the [001] axis through the pyramid’s center and reduces the symmetry of the pyramid from C_{4v} to C_{2v}. This will subsequently lift some degeneracies of hole levels as outlined further below. We note that the piezoelectric potential depends linearly on the QD size and scales like \( V_p \propto L_b \varepsilon_0 \).

In the confinement potential we solve the 3D effective mass (anisotropic masses) single-particle Schrödinger equation using a modified Davidson algorithm [17]. In Fig. 5A the wavefunctions for localized electron and hole levels in a 12 nm quantum pyramid with \{101\} facets are shown. In Fig. 5B the wavefunctions for a pyramid with the same volume but \{203\} side facets are given. The orbitals are for 70% probability to find the particle inside. In (C) and (D), ground state electron and hole wavefunctions, respectively, are compared for a 7 nm and 12 nm pyramid with \{101\} facets.

For \{101\} facets and a base length between 6 and 18 nm only one electron level exists (which can be populated with up to two electrons of opposite spin). For smaller pyramids no localized electron states exist. The hole levels are indexed according to their nodes in the different directions. The \|100\> and \|010\> state would be degenerate if the piezoelectric potential had been neglected. Inclusion of \( V_p \) leads to a size dependent splitting (about 20 meV for \( L_b = 12 \) nm) [17]. Non-degenerate levels are, however, affected only in second order perturbation. Optical transitions are possible between the electron ground state and the hole \|000\> level; the hole \|001\> level has about 50% of the ground state wavefunction overlap and contributes to another allowed transition, which is found in luminescence as described in Section 5. This is particular to the pyramidal geometry and would not occur for a box-like quantum dot.

The comparison of 7 nm and 12 nm quantum pyramids (Figs 5C and D) shows that the extension of the electron wavefunction stays almost constant due to strong tunneling into the barrier in the case of small dots. The hole ground state wavefunction follows more closely the QD shape due to the stronger localization caused by the larger mass.

In the case of \{203\} side facets, the hole wavefunctions extend considerably more into the wetting layer. With respect to \{101\} facets the sequence of the electronic states is changed. Additionally Coulomb forces between electrons and holes can be treated as a perturbation [17]. For \( L_b = 12 \) nm we find an exciton binding energy of 20 meV which is a 20-fold enhancement with respect to the InAs bulk exciton energy of 1 meV. The exciton binding energy is small compared to the kinetic energy in the order of 500 meV for electrons and holes together, thus \textit{a posteriori} justifying the perturbational approach.

In Fig. 6A we compare the ground state transition energy as a function a pyramid base length for pyramids with \{101\} and \{203\} facets. For the same base length the flatter pyramid exhibits the higher energy due to reduced volume. The electron level actually depends in a good approximation on the volume only and not on the facet shape (even an isovolumetric sphere was a good approximation [17]). Hole levels are sensitive to the QD shape. The energy separation between the \|000\> and \|001\> hole states is shown in Fig. 6B for the two different facet types as a function of ground state energy (solid circles are experimental data for various samples and will be discussed below in Section 5). The variation of energy of the excited state with a variation of ground state energy is larger for the \{203\}-facet case. It has a positive slope in both cases, i.e. for increasing ground state energy, the energy of the excited state increases even further. Thus in general we expect the excited transitions to be broadened more strongly than the ground state transition [29].

5. Luminescence experiments

We have shown in [9,14] that single QDs luminescence lines are ultrasharp, similar to atoms, even at elevated temperatures, proving the true zero-dimensional nature of the QDs. In the present paper we
Fig. 6. (A) Ground state transition energy as a function of pyramid base length for \{101\} and \{203\} facets. (B) Separation of \langle 001 \rangle hole level from \langle 000 \rangle ground state as a function of ground state transition energy for a variety of quantum pyramid samples. Solid lines are theoretical results for \{101\} and \{203\} side facets. Samples have been grown under similar conditions, in particular A: T=460°C, t_\text{av}=1.2 nm, B,C,D: T=480°C, t_\text{av}=1.0 nm, E,F: T=480°C, t_\text{av}=1.2 nm, G: T=480°C, t_\text{av}=6 \times (0.1 nm with 100 s annealing).
Fig. 7. (A) PL spectra (T = 8 K, unscaled, semilogarithmic) of t\textsubscript{av} = 1.0 nm QDs for different excitation density D given in W cm\textsuperscript{-2}. Predicted transition energies of excited hole levels are indicated by arrows. (B) Lineshape fit (three Gaussians) to the 500 W cm\textsuperscript{-2} spectrum of part (A), shown in linear scale together with fit parameters. (C) Peak intensity of QD ground state emission at 8 K as a function of excitation density for two samples with t\textsubscript{av} = 1.0 nm and t\textsubscript{av} = 1.2 nm, respectively.

Focus on QD ensemble spectra. Figure 7A depicts a series of luminescence spectra taken at different excitation density on a QD array with well developed pyramids. The intensity of the ground state transition (1.1 eV) increases linearly with a slope close to 1 for increasing excitation density (see Fig. 7C) and starts to saturate at 50 W cm\textsuperscript{-2}, when a second peak appears at 1.17 eV, which we attribute to the transition involving the |001\rangle hole state [30]. Finally a third peak at about 1.24 eV evolves due to the |002\rangle hole state and the hole wetting layer continuum. Figure 7B shows a nearly perfect lineshape fit (linear scale) using three Gaussians to the experimental spectrum. The energy positions agree very well with the hole level scheme we have predicted theoretically. The transitions of ground state electrons with excited holes can also be observed in absorption spectra, as discussed in detail in [30]. The fitted inhomogeneous broadenings of the excited |001\rangle state is larger than that of the ground state luminescence as expected from theory, since \(\frac{\partial E_{001}}{\partial E_{000}} > 0\).

By attributing the inhomogeneous broadening of the ground state transition to size fluctuations only we obtain an upper limit for the size broadening. Using the theoretical dependence of transition energy on pyramid base length L\textsubscript{b} we find a standard variation of \(\sigma_{L_b} = 0.5 \text{ nm}\) for the fit
Fig. 8. QD emission intensity as a function of temperature for $t_{av} = 1.2$ nm with optimal fit to the curve $I/I_0 = 1/(1 + C \exp(-E_a/kT))$ with $E_a = 170$ meV.

value of FWHM = 50 meV. Thus the relative standard deviation, as introduced in [29], is $\xi = 0.04$. For smaller quantum dots, with ground state energy at 1.35 eV ($L_b \approx 7$ nm), the variation of quantum dot size by a single InAs molecule amounts to 0.06 meV and could be resolved experimentally by us [14].

In Fig. 6B we have compiled results from various samples grown under similar conditions (details are given in the figure caption). The separation of the excited hole state from the ground state shows a slight trend (opposite to the theoretical result for fixed dot shape) to increase for decreasing ground state energy. This change is interpreted by us as a change in average dot shape towards a smaller facet angle for larger dots. The observed variation is, however, rather subtle because the changes in energy levels are smaller than the inhomogeneous broadening.

The carrier capture (for above barrier generation) into the QD ground state is observed to be surprisingly efficient since at low excitation density no other luminescence channels are present and the intensity of the QD line is comparable to the emission intensity from very good quantum wells. We like to emphasize that we do not observe luminescence from excited states at low excitation density as had been reported in Bockelmann et al. [31]. In Bockelmann et al. [31] 125 nW laser power (at 1.96 eV) were focused with a spot size of 1.5 $\mu$m diameter on to a single QD of 450 nm base width. This corresponds to an excitation density of $\sim 7$ W cm$^{-2}$. Assuming, as in Bockelmann et al. [31], an exciton lifetime of 100 ps, the steady state carrier density, however, is 40 electron hole pairs. Since the QD area is 10% of the excitation spot, the spectra in Bockelmann et al. [31] thus may not represent the limit of low excitation density.

The luminescence intensity stays almost constant up to 150 K and then decreases with increas-
Fig. 9. Luminescence spectra of QD array (t_{av} = 1.2 nm) excited selectively at 1.165 eV (solid line) and via the GaAs barrier (dotted line).

6. Energy relaxation

So far we have considered only luminescence response upon excitation of carriers in the barrier with energy far above the QD or WL. In this section we discuss a number of experiments involving charge carriers excited with a defined, small (<200 meV) excess energy above the ground state transition. Detailed predictions have been published about the reduced energy relaxation by phonon emission in nanostructures ('phonon bottleneck' effect), especially quantum box systems [32–34]. The basic idea is that phonon relaxation between fully quantized electronic states can occur only if the level separation matches a phonon energy due to the law of energy conservation. LO and LO + LA emission have been considered. In the following we will show that the energy is conserved in our structures via multi-phonon relaxation which allows for a variety of phonon energies to contribute to energy relaxation [18].

The first key experiment is the selectively excited luminescence (SEL) spectrum (fixed excitation wavelength 1064 nm) (Fig. 9) of a typical quantum pyramid ensemble. The spectrum exhibits several peaks grouped around 1, 2 and 3 LO phonon energies; the envelope of the spectrum follows the inhomogeneous broadening of the regular PL peak. Based on known bulk phonon energies and model calculations for strained pyramids [17] we have identified various phonons (GaAs barrier
InAs/GaAs
T = 1.8 K

Fig. 10. PLE spectra of the QD luminescence (scaled to same height of peak C). The detection energies are indicated by crosses. Dotted line is PL spectrum upon above barrier excitation.

(36.6 meV), InAs wetting layer (29.5 meV [35]), InAs QD (31.9 meV) and interface mode (35.0 meV) as the cause of the peaks. We emphasize that the different peaks are all due to different QDs (of different ground state energy). Two conclusions can be drawn: (i) luminescence response is enhanced when the condition for relaxation with a particular possible phonon energy is fulfilled for a particular dot; (ii) a number of different phonons contribute and due to the contribution of various optical and additionally acoustic phonons [18] the peaks merge to a continuum, thus allowing for efficient relaxation over an energy band.

A slightly different access to the relaxation of carriers is obtained with photoluminescence excitation (PLE) spectroscopy. In this experiment the detection energy is fixed and the excitation light energy is tuned across the high energy side. This means that the PLE spectrum belongs to QDs with exactly the same ground state energy. However, for a given ground state energy, shape fluctuations vary the level energies for excited states. Thus the PLE spectrum at different energies is in general still due to response of different dots (with the same ground state energy). The PLE technique has been widely-used to reveal excited electronic states in quantum wells and wires, e.g. [36]. At first surprisingly, the PLE spectra of our quantum dots (Fig. 10) show a multi-peak structure which cannot be interpreted to origin from excited electronic states. We previously reported the observation
Fig. 11. Energy differences between PLE peaks and detection energy for various detection energies. Solid lines are theoretical hole level energies (for \{101\} side facets).

of a series of three almost equidistant peaks whose separation does not change with the detection energy (Fig. 11) at the high energy side of the detection energy [6]. Since any higher electronic level has a characteristic dependence on the ground state energy (i.e. basically the QD volume), as shown as lines in Fig. 11, these peaks do not simply relate to excited electronic levels in the QD as claimed in Ref. [37]. Their constant energy separation leads us to the conclusion that they are due to multi-phonon emission processes which involve 1, 2 or 3 LO phonons. This also corresponds to the SEL spectra discussed before. The 3 LO resonance is strongest due to the fact that it is nearly resonant with the allowed transition into the \{001\} excited hole state. Averaging of the PLE spectra over the detection wavelength reveals a peak at the position of the \{001\} hole level. The PLE peak at 1.39 eV does not depend on the detection wavelength and is assigned, in agreement with absorption spectra [9,30], to the wetting layer ground state.

We note that the PLE spectrum becomes broad and rather structureless for excess energies larger than 150 meV. According to our calculations this is the typical localization energy for electrons and also for holes in the QDs [17]. Thus the continuum onset in PLE is due to excitation into the
wetting layer. We note that for small QDs (prepared with kinetically limited growth [9,14,19]) with a ground state energy around 1.35 eV (size L ≈ 7 nm) no LO resonances are observed in PLE because the electron level exhibits so weak localization that the continuum onset starts already close to (about 30–40 meV above) the detection energy.

7. Conclusion

We have prepared dense, laterally ordered arrays of quantum pyramids with narrow size distribution (relative standard deviation of size broadening ξ ≈ 0.04). Strain distribution and electronic states have been modelled numerically. Excited states are revealed only when the ground state luminescence strongly saturates. The excited levels in the luminescence spectra agree with our theoretical calculations for pyramid facets between {101} and {203} and are due to allowed transitions between excited hole states with the only electron (ground) state in the QD. The observed enhanced broadening of the higher transition is expected from theory.

The energy relaxation for excitation into the zero-dimensional density of QD states is dominated by the phonon energy selection rule. Energy relaxation is possible with multi-phonon or multiple phonon processes, thus increasing the number of possible relaxation channels. A phonon bottleneck effect does not exist. Relaxation into the QD ground state occurs fast upon excitation in the wetting layer or in the barrier.

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References


[22] The same is true for a 2D confined object (quantum wire) and 1D confined object (quantum well).

[23] This simple case has been treated many times in the literature. Compressive inplane stress $\varepsilon_Q$ due to lattice mismatch leads to expansion perpendicular to the interface $\varepsilon_o = -2\varepsilon_Q/m$, $m$ being the Poisson ratio. For $v = 1/3$, $\varepsilon_o = -\varepsilon_Q$.


[28] Animations of the piezoelectric potential and some wavefunctions can be found on our WWW server at http://sol.physik.tu-berlin.de/.


