Electronic Properties of InAs/GaAs Quantum Dots

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We report a detailed study of the electronic properties of self-organized InAs/GaAs quantum dots (QDs) by photoluminescence (PL), time-resolved PL, and PL excitation (PLE) experiments. High-quality InAs/GaAs QDs of tunable size were obtained using the variable deposition amount approach in MBE-growth, yielding ultimately room-temperature emission at 1.3 µm for island area densities of ~400 µm⁻². The experiments emphasize the role of a slowed down carrier relaxation in the QDs, being important e.g. for energy transfer processes between QDs and the temperature dependence of the carrier capture processes. The quantum size effect of the excited state spectrum is revealed in PLE experiments and shown to be in good agreement to numerical results for pyramidal QDs based on 8 band $k \cdot p$ theory. Finally, phonon-assisted recombination processes are identified demonstrating an enhanced exciton-LO-phonon coupling. Excellent agreement with estimations in the adiabatic approximation suggests that this enhancement is the consequence of the particular quantum confinement and the piezoelectricity in the strained low-symmetry QDs.

I. INTRODUCTION

The formation of nanoscale coherent islands in highly strained semiconductor epitaxy has been extensively studied as means to generate optically active quantum dots (QDs) [1]. In spite of the large size inhomogeneity [2-5] of ~10% such Stranski-Krastanow QDs have been successfully employed in devices [6-10], demonstrating partly the predicted advantages of QD-based devices [11,12]. Though self-organized QDs are easily incorporated in conventional device structures, the interdependent nature of the QD density and size makes

the adaptation of the QDs to the device needs difficult. Additionally, the inhomogeneous broadening of the discrete density of states for self-organized QD ensembles hampers detailed investigations of the excited state spectrum and of energy relaxation (and recombination) processes, which are both of basic physical interest and critical for design and performance of devices. In fact, it is often necessary to distinguish between extrinsic ensemble effects and intrinsic properties of single QDs, e.g. in describing the carrier dynamics [13,14]. In recent years, extensive work has been devoted to the study of the excited states, as well as the temperature dependence and dynamical behavior of the optical properties of self-organized QDs [4,6,15-27]. Furthermore, the prediction [28] of slowed-down carrier relaxation due to restricted inelastic phonon scattering in QDs was evidenced by the observation of multi-phonon resonances in photoluminescence excitation (PLE) spectra [24,29-31]. However, the electronic properties of such self-organized QDs are still controversially discussed owing to the inhomogeneous broadening and the wide spread of reported structural properties of the individual QDs. Further progress in the understanding of the electronic properties of the self-organized QDs might be stimulated by improved samples.

In this paper, we review optical investigations of a new class of self-organized InAs/GaAs QD samples giving improved insight into the electronic properties of such QDs. The samples were grown in the variable deposition amount (VDA) approach [32] exploiting the concept of vertical stacking [33] to control the island formation process. A suitable seed layer and the InAs deposition amount in the second layer (O₂) are used to control, respectively, the island density and size for given growth conditions. Additionally, the island size distribution is improved in this growth approach enabling the realization of full widths at half maximum (FWHMs) down to 18meV. The VDA approach allows for high-quality high-density InAs QDs emitting at 1.3μm at room temperature [32,34] and new studies, e.g., of nonresonant energy transfer processes between neighboring QDs [35,36]. In the following, we will describe photoluminescence (PL), PLE, and time-resolved PL (TRPL) results for samples with widely varying carrier localization as a function of temperature. The results give insight into the carrier dynamics as well as the excited state spectrum of self-organized InAs/GaAs QDs. The experimental results are discussed based on 8 band kp calculations for pyramidal InAs/GaAs QDs [37]. We find that the seed QDs in the VDA samples allows to tune the QD size and improve the size and shape uniformity of the optically active QDs, whereas the effect on their electronic properties is negligible.

II. EXPERIMENTAL

The investigated InAs/GaAs QD samples were grown by molecular beam epitaxy on semi-insulating GaAs(001) substrates. InAs was deposited at 500°C, an As₄ partial pressure of 6×10⁻⁶Torr, and a growth rate of 0.22MLs⁻¹. Special care was taken in capping the InAs QDs in order to maintain the island shape and minimize In/Ga interdiffusion. Therefore, after the InAs deposition the sample temperature was lowered to 400°C for the deposition of the GaAs cap layer using migration enhanced epitaxy (MEE) as described in Refs. [4] and [32]. Here we report results for single-layer samples and a variety of bilayer VDA samples with a 1.74ML seed layer and 36 to 54ML MEE-grown GaAs spacer layer all grown under the same growth conditions. The VDA growth approach provides enhanced control of the island formation process [32]. Figure 1(e) shows a schematic of the VDA growth approach, which exploits the well-established tendency of islands to form vertical stacks in multi-layered structures due to the modulated surface strain (σsurface) induced by the buried islands [33]. However, in contrast to previous attempts to generate a high density of identical islands in multi-layered samples [25,38-40], here the islands in the first layer (dubbed seed layer) are
used to control the island density in the second layer. Then, the in general different InAs deposition $\Theta_2$ in the second layer (and therewith the InAs amount available for each island) allows controlled tuning of the average islands size in the second layer for given growth conditions. Additionally, the VDA samples benefit from an improved uniformity of the island ensemble [32].

Panels 1(a)-(d) of Fig. 1 show cross-sectional transmission electron microscopy (TEM) images of the 1.74ML seed layer ($\Theta_2=0$) and three VDA samples with $\Theta_2=1.74$, 2.00, and 3.00ML, respectively, and 36ML spacers. The 36 ML spacer ensures almost perfect vertical alignment in QD pairs even for largely mismatched InAs depositions in the seed and the second layer in good agreement with previous observations for symmetric depositions [33]. The strain contrast of the islands in the second layer increases with increasing $\Theta_2$ indicating an increasing island size. Finally, even for the 3.00ML VDA sample, having the largest islands, we find only very few defected islands. More quantitative information on the islands was obtained from AFM investigations for identically grown but uncapped samples [32]. (Note that the growth of capped samples deviates only after the initial cooling down to 400°C.) The AFM investigations yielded a QD density of $3.8 \times 10^{10}$ cm$^{-2}$ (4.8 $\times 10^{10}$ cm$^{-2}$), an average height of $(38 \pm 9)$ Å (97 $\pm 7$ Å), and an average width of $(169 \pm 18)$ Å (256 $\pm 12$ Å) for the 1.74ML single-layer {3.00ML VDA} sample [32]. The AFM results indicate improved island uniformity in the VDA sample. Note, that the AFM measurements overestimate the lateral extension of the islands. Cross-sectional TEM images (not shown) for the uncapped 3.00ML VDA sample indicate an average island baselength of ~19nm.

The PL and PLE measurements were performed in a continuous-flow He-cryostat, providing temperatures between 3.5 and 360K. PL was excited either by an Ar$^+$ laser or a tungsten lamp dispersed by a 0.27m double-grating monochromator as tunable, low excitation density (<0.02Wcm$^{-2}$) light source. The PL was dispersed in a double-grating monochromator and detected by a cooled Ge-diode (North Coast 817L). Time-resolved PL was excited by 6ps pulses of a synchronously pumped dye-laser at 670nm in the GaAs barrier, spectrally dispersed by a 0.35m subtractive double-grating monochromator, and detected with a multi-channel plate multiplier with a S1-cathode in photon-counting mode. The system response with a FWHM of ~50 ps was taken into account in the analysis of the transients.
III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 depicts PL spectra of typical samples grown in the VDA approach. The inset compares PL spectra of the series of samples for which TEM images are shown in Fig. 1 revealing the influence of the InAs deposition amount $\Theta_2$ in the second layer. At low excitation densities all samples show only a single PL peak attributed to the QD ground state transition. For the 1.74ML seed layer sample ($\Theta_2 = 0$) the PL peak is centered at 1.175eV and has a FWHM of 75meV. Increasing $\Theta_2$ to 3.00ML, the transition energy is decreased to 1.028eV with an improved FWHM of 25meV. This behavior closely reflects the evolution of the structural properties of the islands in the second layer as observed in AFM and TEM investigations. Although the VDA samples contain asymmetric (with respect to size) QD pairs (AQDPs), see Fig. 1, obviously only the larger QD in the second layer is optically active. As will be shown below, the 36ML spacer leads to energy transfer processes in the AQDPs, which efficiently quench the luminescence of the smaller seed QDs [35].

The main part of Fig. 2 depicts PL and PLE spectra of a second 3.00ML VDA sample on a semilogarithmic scale. The practically matching ground state transition energy (1.024eV) demonstrates the excellent reproducibility of this growth approach and the FWHM of only 18meV of the almost Gaussian PL peak is the lowest one we obtained yet. Note that semilogarithmic PL spectra reveal for most samples a weak but extended high-energy shoulder. TRPL investigations indicate this luminescence to originate from the ground state transition of smaller QDs, i.e. the seed QDs and/or (as indicated by some AFM data [32]) also a small number of unpaired islands in the second layer. More information on excited states, the wetting layer (WL), and relaxation processes are provided by PLE investigations. Figure 2 shows a typical PLE spectrum recorded at the PL maximum, which reveals localized excitation via a series of intradot excited state transitions for $E<1.4eV$ as well as efficient delocalized excitation via the WL and the GaAs barrier [25]. The WL energy of 1.445eV is typical for the employed growth conditions and corresponds to an ~1ML thick InAs quantum well [41]. For the growth conditions used, the stacking process only marginally affects the WL transition energy and, therefore, the morphology of the WL in the second layer. The varying ground state transition energy of the QDs (inset of Fig. 2) reflects the variation of the exciton localization with respect to the WL ranging from 270meV for the 1.74ML seed layer to 430meV for the 3.00ML VDA sample.

In the following, the various aspects of the PL and PLE spectra shown in Fig. 2 are discussed in detail for a variety of single layer and VDA samples providing new insight into the electronic properties of self-organized InAs/GaAs QDs. The experimental data are compared to results of numerical calculations of the electronic states of pyramidal InAs/GaAs QDs on the basis of the 8 band $k\cdot p$ model described in detail in Ref. [37].
III.1 Energy Transfer Processes  

As shown above the (Fig. 1) VDA growth approach generates well-defined AQDPs, for which the ground state transition energies of both constituents are clearly distinguishable. The VDA samples show, however, only a single PL peak, while the expected PL of the smaller seed-layer QDs (SQDs) at \(~1.2\text{eV}\) is missing or at least 2 orders of magnitude weaker than the lower energy PL peak, Fig. 2. Obviously, only the larger QDs (LQDs) in the second layer are optically active and efficient energy transfer processes within the AQDPs quench the luminescence of SQDs \[35,36\]. Similar energy transfer processes have been reported for mixtures of differently sized colloidal QDs and attributed to dipolar long-range resonance transfer \[42\], whereby the interdot separation was varied via the surface passivation layer. For the AQDPs the interdot separation is controlled on a ML-scale by the grown GaAs spacer thickness.

Figure 3 compares PL spectra for a series of 2.00ML VDA samples with GaAs spacers of 36, 45, and 54ML thickness. The PL spectrum of the 36ML sample shows only one, almost Gaussian, peak at 1.102eV with a FWHM of 58meV. With increasing spacer thickness an additional PL peak becomes evident on the high-energy side at \(~1.21\text{eV}\), resulting in a clear double peak structure for the 54ML spacer sample. Both, excitation in the GaAs barrier as well as in the WL yield similar results but show a small preference of SQDs in the former case. For GaAs excitation the majority of carriers is generated on the substrate side of the QD layers and favorably captured by the SQDs ‘masking’ the LQDs. PLE measurements (not shown here) demonstrate that the energy transfer processes take indeed place between localized QD states, i.e., the carriers are first captured into the SQDs before they are efficiently transferred to the LQDs. The increase of the PL yield of the SQDs with increasing spacer thickness is attributed to the decreasing excitation transfer probability with increasing tunnel barrier thickness. Note that the actual tunnel barrier width is much smaller than the grown spacer thickness, since the 3D-seed islands significantly protrude into the spacer. We identify the actual tunnel barrier with the separation between the seed island tip and the second InAs layer, which can be estimated based on AFM data for the seed islands to range from \(~5.8\) to \(~11\)nm for the investigated spacer thicknesses. The ratio of the integrated intensities of PL from SQDs and LQDs allows to estimate the transfer efficiency \(\eta\), ranging from nearly 100% for 36ML spacer down to \(~15\)% for the 54ML spacer \[35\].

As a result of the statistical fluctuations in island size and shape, we have to assume that in general the eigenstates of the SQD and LQD in the AQDPs are nonresonant. Furthermore, slowed-down intradot carrier relaxation \[25,43\] on the time scale of some 10ps might prevent carriers to reach the ground state in the SQDs before energy transfer takes place. TRPL investigations of the series of 2.00ML VDA samples with various spacer thicknesses give further insight into the energy transfer mechanisms in the AQDPs. The transients have been recorded at low excitation densities for which all state filling effects could be neglected. The
transients recorded for various detection energies in the regions of PL from SQDs (>~1.16eV) and LQDs (<~1.16eV) are well fitted by an exponential rise and decay convoluted with the system response function giving a resolution of ~10ps for the PL rise times. Figure 4 depicts the PL rise (a) and decay (b) times as a function of the detection energy. Surprisingly, the decay time is practically independent of the detection energy and the spacer thickness. For symmetrically stacked samples grown under the same conditions also almost size-independent recombination times have been observed and attributed to the fact that the investigated QDs are close to the strong confinement regime [25]. However, the energy transfer processes, which efficiently quench the SQD PL yield, should be manifest in a pronounced but spacer thickness dependent decrease of the SQD decay time, which is not observed. Obviously, the excitation channel and not the SQD ground state itself is affected by the energy transfer processes in good agreement with the predicted strong vertical localization of the ground state wavefunction [37]. On the contrary, the PL rise time, describing carrier diffusion and relaxation processes, shows a characteristic spacer-dependent evolution. For the 36ML and 45ML spacer samples the rise time is much shorter for SQDs than LQDs, whereas no such difference is observed for the 54ML spacer. The finite rise time (~30ps) of the SQD PL observed for thin spacers is tentatively attributed to carrier diffusion processes. Obviously, the energy transfer processes compete with intradot carrier relaxation and, thus, originate from excited states of the QDs. The observed efficient excitation transfer in the AQDPs is therefore closely connected to the slowed-down relaxation processes in the QDs.

Further information on the nature of the energy transfer processes is obtained from the long term dynamics of the QD PL. For samples with intermediate transfer yield, an additional slow decay component on a 10ns time scale is observed. Typical transients are shown in Fig. 5 for a 2.00ML VDA sample with 45ML spacer, whereby 16ML GaAs spacer have been replaced by AlGaAs to increase the tunnel barrier. A possible explanation for the second slow decay component of the LQD PL might be separate transfer of the electron and hole on...
different time scales. The PL yield of the SQDs is determined by the transfer of the faster carrier, forming an intermediate spatially indirect exciton state with the electron and hole in different QDs. The limited wavefunction overlap in such a spatially indirect exciton leads to a negligible recombination probability. The slower transfer of the second carrier determines the long living PL of the LQDs. Calculated eigenstate spectra and the corresponding wavefunctions suggest that most likely electron transfer is much faster than hole transfer. On one hand, the electron wavefunctions are less localized in the growth direction and, on the other hand, the hole states have smaller substate splittings allowing for faster relaxation. From the experimental data on the vertical energy transfer processes we estimate that for the investigated samples lateral energy transfer processes should become important only for QD sheet densities well above $2 \times 10^{11} \text{cm}^{-2}$ [35]. However, it is not clear yet how the transfer probability scales with the localization energy and therefore the QD size.

### III.2 Temperature Dependence

One main driving force for device applications of QDs is the temperature-stability of their properties resulting from the combination of the discrete density of states and a potentially large substate splitting. As shown in the inset of Fig. 2 the VDA growth approach allows to grow for one and the same growth conditions and comparable island densities QD samples with different carrier localization energies. In the following we will compare properties of the 1.74ML seed layer and the 3.00ML VDA samples, which are governed by ensemble and intrinsic properties, respectively. Both samples are distinguished by the relative broadening of the exciton localization energy, which is much larger for the 1.74ML sample (27%) than for the 3.00ML (5.8%) sample.

Figure 6 shows PL spectra of the 1.74ML single layer (panel (a)) and the 3.00ML VDA (panel (b)) samples for various temperatures. The QDs in the 3.00ML VDA sample show narrower and more temperature stable PL than the seed QDs as a result of their larger size and better uniformity. These PL spectra provide information on a variety of ensemble and intrinsic properties of the QDs, which will be discussed in more detail below. The main features are the temperature dependencies of the PL energy and FWHM, the integrated PL intensity and the appearance of a high-energy sideband with increasing temperature. Note that the large QDs with an area density of $\sim 4 \times 10^{10} \text{cm}^{-2}$ obtained in the VDA approach emit at 1.3µm (FWHM=29meV) at room temperature; a wavelength of fundamental importance to fiber optic communications.

Figure 7 depicts the energy (solid dots) and FWHM (open diamonds) of the QD ground state transition for the 1.74ML single layer (panel (a)) and the 3.00ML VDA (panel (b)) samples as a function of temperature, demonstrating a qualitatively different behavior. For the

![Fig. 6: PL spectra for the 1.74ML (a) and the 3.00ML VDA (b) for various sample temperatures and an excitation density of 0.5Wcm$^{-2}$.

(a) θ=1.74ML

(b) θ=1.74ML+3.00ML

l$_{q}$=0.5Wcm$^{-2}$

T=6.5K

T=40K

T=90K

T=150K

T=215K

T=280K

T=300K

*500

*20

*5

*200

$1.0$  $1.1$  $1.2$  $1.3$  $1.4$  $0.9$  $1.0$  $1.1$  $1.2$  $1.3$

Energy (eV)
1.74ML sample the FWHM decreases by ~30% for temperatures above ~80K and the ground state transition energy shows a simultaneous low-energy shift. We interpret this behavior as an ensemble effect, which indicates preferential quenching of luminescence from the smaller QDs in the ensemble, providing less carrier localization [21,22]. Such preferential quenching is obviously negligible for the more homogeneous 3.00ML VDA sample, for which the FWHM increases slightly up to ~120K and the ground state transition shifts smoothly to lower energies. The uniformity of the QD ensemble in this sample enables the intrinsic properties of the single QDs to dominate the temperature dependencies even if the experiment probes the inhomogeneous ensemble. The slight increase of the FWHM observed for temperatures up to 120K is attributed to the thermal population of excited hole states expected a few meV above the ground state [37]. We note that the low-energy tail of the QD PL peak maintains its shape over at least two orders of magnitude (compare Fig. 2 for a semilogarithmic plot). Obviously, the inhomogeneous broadening dominates for temperatures up to 360K and fits assuming a Voigt profile centered at the peak maximum place an upper limit of ~4meV on the FWHM of the Lorentz contribution of single QDs at room temperature. At temperatures below 50K FWHMs of less than 150µeV have been reported for the homogeneous PL lines of single QDs [44,45]. Phonon scattering processes are, however, expected to cause much larger homogeneous FWHMs at higher temperatures [46].

The temperature-dependent energy shift of bulk bandgaps is phenomenologically described by Varshni’s formula [47]. The full line in panel (b) of Fig. 7 represents a corresponding fit to the transition energy in the 3.00ML VDA sample. The temperature dependent shift falls in between of those of the bulk InAs (dotted line) and GaAs (dashed line) bandgaps, which are expected to be the limits for large and small QDs, respectively. For the 1.74ML sample the dominant ensemble effects make a straightforward fit of the energy data meaningless. However, both the low and high temperature regions are well described by the temperature dependent shift observed for the 3.00ML VDA sample (full lines in panel (a)), whereas in the intermediate region ensemble effects prevail and enhance the temperature dependent redshift. A detailed understanding of the temperature-dependence of the ground state transition energy of the self-organized InAs/GaAs QDs would require numerical calculations with temperature-dependent material parameters, which are not available yet.

The temperature evolution of the integrated QD PL intensity is depicted by solid dots in Fig. 8 for the 1.74ML (panel (a)) and 3.00ML (panel (b)) samples. The intensity begins to

Fig. 7: FWHM (diamonds) and energy (dots) of the ground state PL for the 1.74ML (a) and the 3.00ML VDA (b). The temperature change of the bulk InAs and GaAs bandgaps are depicted by the dotted and dashed lines in panel (b), respectively. Full lines show the variation of the QD ground state transition energy in the 3.00ML sample fitted by Varshni’s formula [47].
decrease above ~100K in good agreement with the observed onset of preferential quenching of the smallest QDs in the 1.74ML sample. Above ~200K the intensity-decrease becomes steeper. The integrated intensity is well-fitted (full lines) assuming two thermally activated nonradiative recombination processes. The obtained activation energies are close to the excited state splitting observed in high-density PL spectra and the localization energy of the ground state exciton with respect to the WL, respectively. However, we emphasize caution in interpreting these activation energies. PLE spectra of the 3.00ML VDA sample (inset of Fig. 8(b)) show a much stronger quenching of the efficiency for nonresonant (GaAs and WL) excitation compared to near-resonant excitation via excited state transitions. Obviously, the decrease of the capture efficiency with increasing temperature dominates the quenching of the PL intensity upon nonresonant excitation. A similar behavior has been observed for smaller QDs, too [25].

This effect becomes quite obvious comparing the integrated PL intensity with the lifetime of the ground state exciton measured upon nonresonant excitation, open diamonds in Fig. 8. The exciton decay monitors the actual ground state population and does not depend on the initial population yield. Below ~100K the PL decay time is practically independent of temperature and QD size, being (790±50)ps and (840±50)ps (indicated by dotted lines), respectively, for the 1.74ML single layer (panel (a)) and the 3.00ML VDA (panel (b)) samples. Above ~100K the lifetime increases up to ~1600ps before it finally starts to decrease. The radiative recombination probability of a given exciton transition is temperature-independent, accounting for the constant lifetime observed at low temperatures when the substate splitting is sufficiently large to prevent significant excited state population. With increasing temperature, however, thermal population of excited states becomes important, resulting in an effective lifetime, which depends on the oscillator strength of the excited state transitions. The hole states are much narrower spaced than the electron states [37] and, thus, populated first, which together with the low probability of transitions between exited hole states and the electron ground state explains the increase of the effective lifetime. Finally, thermally induced escape will dominate reducing the lifetime again. Qualitatively similar results for smaller QDs with ~120meV exciton localization have been successfully simulated considering one localized exciton state and delocalized WL states [48]. In the present case, however, a complete simulation is hampered by the need to include a spectrum of excited state transitions. Fits of the exciton lifetime assuming a constant
radiative lifetime ($\tau_{\text{rad}}=1600\text{ps}$) and complete nonradiative recombination for carriers activated to the barrier yields activation energies $E_{\tau}$ of $(170\pm30)\text{meV}$ and $(240\pm30)\text{meV}$, respectively, for the 1.74ML and the 3.00ML sample. These activation energies indicate electron evaporation to the WL to be the driving mechanism behind the decreasing exciton lifetime. Indeed, owing to the fact that the exciton binding energy of $\sim20\text{meV}$ in the QDs [37] is much smaller than the carrier localization energies, single carrier escape might be expected to dominate. Room temperature (300K) lifetimes of $\sim35$ and $\sim150\text{ps}$ are estimated, respectively, which practically correspond to the electron escape times.

Mukai et al. [19] proposed thermally activated nonradiative recombination in the barrier to explain the decreasing excitation efficiency of the QD PL in their samples. The activation energies were thereby characteristic for the nonradiative recombination centers. The present experimental results, however, suggest the carrier capture probability itself to be temperature dependent, i.e. to decrease with increasing temperature. A possible reason might be the slowed-down carrier relaxation in QDs, allowing thermally induced escape to dominate intradot relaxation for carriers captured into excited states, thus reducing the capture efficiency. Finally, the PLE spectra (inset of Fig. 8(b)) for the 3.00ML sample demonstrate size-selective excitation at temperatures as high as 250K, well above the regime where lateral exciton transfer should become important. Efficient carrier loss due to surface recombination and diffusion into the substrate prevent lateral coupling of the QDs, which would be a precondition for the formation of a common Fermi-level for the QD ensemble. Placing the active QD region between two AlGaAs diffusion barriers should suppress such loss mechanisms and increase the temperature stability of the QD PL intensity.

### III.3 Local-Equilibrium Emission

The self-organized InAs/GaAs QDs provide strong carrier localization and a high temperature stability of the PL intensity, enabling the exploitation of the thermal population of excited QD states in the optical investigation of their electronic properties. Figure 9 depicts normalized PL spectra for the 3.00ML VDA sample with respect to the energy of the peak maximum for temperatures up to 360K in order to compare the lineshapes. In addition to the slight broadening of the ground state peak $I_g$ the excited state transition $I^*$ becomes visible shifted $\sim72\text{meV}$ to higher energies for temperatures above $\sim180K$. At this stage the thermal population of the excited electron and hole states becomes significant enough to resolve corresponding transitions in the PL spectra. The inset of Fig. 9 depicts the intensity ratio $I^*/I_g$ over the inverse temperature. The full line represents a fit to the intensity ratio assuming a three-level model with the degeneracies $g_i$ and oscillator strengths $f_i$, yielding an activation energy of

![Fig. 9: Normalized PL spectra for the 3.00ML VDA sample for various temperatures. The insert shows the intensity ratio $I^*/I_g$ on a semilogarithmic scale together with an exponential fit.](image-url)
(70±5)meV and a weighting factor \( g^*f^*/gfg \) of 1.7. The activation energy corresponds to the energy shift between the ground and excited state transitions and to the weighting factor contribute a number of superimposed excited state transitions as well as a possibly higher oscillator strength of some of the excited state transitions [37]. Although the electronic structure of the QDs is more complex than the assumed three-level model (e.g., excited electron and hole levels are involved), Fig. 9 demonstrates a local equilibrium distribution of carriers between ground and excited states for each single QD.

The resolution of the nonresonantly excited PL spectra (Fig. 2) is limited by inhomogeneous broadening, i.e., the nonuniformity of the QD ensemble. Size-selective PLE spectra (e.g., Fig. 2) show, however, rich finestructure in the near resonant excitation regime, suggesting that, e.g., in high-density PL spectra [49,50,51] the electronic finestructure of the QDs is masked. The interpretation of the PLE spectra, which involve excited state absorption and carrier relaxation processes, is, however, ambiguous in the case of QDs. On one hand, since the self-organized InAs/GaAs QDs vary in size and shape the QD excited state spectrum of QDs with the same ground state transition energy (\( E_{\text{det}} \)) is generally inhomogeneously broadened, limiting the resolution in PLE experiments [25]. On the other hand, the slowed down carrier relaxation makes the QDs prone to possible nonradiative recombination processes, the so-called ‘phonon-bottleneck’ effect [28]. Both effects together might lead to the occurrence of multi-LO-phonon resonances in PLE spectra, which indeed have been observed recently [29-31], demonstrating inelastic phonon scattering as the dominant relaxation process [24]. TRPL measurements show the extrinsic nature of the competing recombination processes, most likely nonradiative recombination at defects in the vicinity of the QDs, i.e., in the low-temperature GaAs barrier. Avoiding such nonradiative recombination by optimization of the growth of the GaAs cap layer has been proposed to allow the unhampered resolution of excited state transitions in the PLE spectra [25,52].

Here, we propose to take advantage of the thermal population of excited QD states upon resonant excitation of the ground state to investigate the ground state transition as well as the excited state spectrum of the QDs in more detail. Figure 10 shows optical spectra for the 3.00ML VDA sample at an elevated sample temperature of \( T=190K \). Panel (a) shows nonresonantly excited PL and PLE detected in the maximum of the PL spectrum. Panel (b) depicts ‘anti-Stokes’ PL excited in the ground state transition (0.990eV) and PLE spectrum for an excited state transition (1.067eV). The dots in panel (a) (dubbed ‘absorption’) show the resonantly excited PL spectrum divided by the thermal carrier distribution \( \exp(-\Delta E/kT) \) in QDs occupied with one exciton.

**Fig. 10:** PL (full lines) and PLE (dashed lines) spectra for the 3.00ML VDA sample at 190K. Panel (a) shows nonresonantly excited PL and PLE detected in the maximum of the PL spectrum. Panel (b) depicts ‘anti-Stokes’ PL excited in the ground state transition (0.990eV) and PLE spectrum for an excited state transition (1.067eV). The dots in panel (a) (dubbed ‘absorption’) show the resonantly excited PL spectrum divided by the thermal carrier distribution \( \exp(-\Delta E/kT) \) in QDs occupied with one exciton.
clearly shows the excited state transition at \( \sim 1.065\text{eV} \), whereas the size-selective PLE spectrum reveals a richer finestructure with the most intense excitation resonance at 1.067eV close to the excited state PL peak position. For such conventional spectra the excitation energy is larger than the detection energy.

Panel (b) in Fig. 10 compares PL (full line) and PLE (dashed line) spectra where the excitation energy is smaller than the detection energy. Thus, the excitons are excited in the QD ground state and subsequent thermal excitation into excited states leads to the detected excited state luminescence. Exciting resonantly the ground state transition \( (E_{\text{exc}}=0.990\text{eV}) \), a series of weak luminescence structures is observed on the high-energy side of the ground state transition, which in nonresonantly excited PL spectra (panel (a)) are lumped together in one excited state transition peak. These lines are attributed to recombination involving various excited states of the selectively excited QD subensemble. The PLE spectrum of the excited state transition at 1.067eV reveals the ground state absorption at 0.993meV. The 3meV high-energy shift with respect to the PL maximum is attributed to the exponential modulation caused by the thermal carrier distribution favoring the PL of QDs with a smaller substate splitting, i.e., higher ground state transition energy. This effect is more obvious in Figure 11(b), which shows a series of PLE spectra recorded at \( T=190\text{K} \) for different detection energies as indicated by arrows in panel (a). The excitation resonances show a redshift with decreasing detection energy indicating size-selective excitation of the ground state transition. Most PLE spectra reveal a doublet structure separated by \( \sim 15\text{meV} \), which is slightly smaller than the separation of the two dominating excited state transitions (\( \sim 20\text{meV} \), PLE spectrum in panel (a)). The doublet structure results from ground state excitation of different sized QDs with one of these two excited state transitions in resonance with the detection energy. Thus, the different energy splitting observed is the result of the QD size dependence of the excited state splitting.

For the PLE spectrum of the ground state transition (dashed line in Fig. 10(a)) and the resonantly excited PL spectrum (solid line in Fig. 10(b)) the roles of excitation and detection are somewhat reversed. PLE probes the excited state absorption spectrum, but might be modified by restricted carrier relaxation processes and carrier localization at defects, whereas the PL spectrum is given by the absorption spectrum modified by the thermal carrier distribution among the localized QD states. The ‘absorption’ spectrum, extracted by dividing the resonantly excited PL by the thermal population distribution \( \exp(-E_{\text{exc}}-E_{\text{det}})/kT) \) for QDs occupied by one exciton, is given by the dotted spectrum in Fig. 10(a). The ‘absorption’ spectrum is found to reproduce the PLE spectrum within the experimental accuracy. For the investigated samples the PLE spectrum indeed follows the absorption spectrum of a subensemble defined by the ground state transition energy unhampered by the slowed down carrier relaxation dynamics. Additionally, the ground state absorption and emission energies

![Fig. 11: (a) PL and PLE spectra for the 3.00ML VDA sample at 190K. Panel (b) depicts ‘anti-Stokes’ PLE spectra for various detection energies (marked by arrows in panel (a)).](image)
are obviously perfectly matched for the self-organized InAs/GaAs QDs, demonstrating the intrinsic nature of the exciton recombination. Finally, the near resonant fine-structure observed in the PLE spectra is practically unchanged for temperatures between 7 and 250K (inset of Fig. 8(b)), suggesting carrier scattering between the different localized QD states to be faster than competing recombination processes even at low temperatures. Fig. 10 shows, thus, that PLE spectroscopy gives reliable access to the excited state spectrum of the QDs, providing high-quality samples with negligible nonradiative recombination.

III.4 Excited State Transitions

As outlined in the previous section, PLE spectroscopy presents for the investigated samples an ideal tool to study size-selectively the excited state transition spectrum of the QDs. Varying the detection energy over the PL peak QDs of different average size are probed, enabling the measurement of the size-dependence of the excited state spectrum for one sample exploiting the inhomogeneous broadening. Figure 12 shows for the 3.00ML VDA sample a contour plot of the PL intensity as a function of the detection energy and the excess excitation energy $\Delta E = E_{\text{exc}} - E_{\text{det}}$ at 7K. The PL intensity is given on a logarithmic scale. For the various excitation resonances the energy shift $\Delta E$, corresponding to the combined excited state energy of the involved electron and hole states (with respect to the respective ground state energy), depends clearly on the detection energy and, therefore, the QD size. For example, with decreasing detection energy $\Delta E$ decreases from 101 to 70meV for the dominating excitation resonance. The decrease of $\Delta E$ with decreasing detection energy demonstrates the quantum-size effect of the excited state splitting for the self-organized InAs/GaAs QDs, supporting the notion of the PLE spectra revealing the absorption spectrum. The single exemption is the resonance at ~35meV, for which $\Delta E$ is independent of the detection energy indicating phonon-assisted absorption as discussed in the next section. The various excitation resonances have FWHMs \( \geq 10\text{meV} \), which are not limited by the experimental resolution (~4meV). The combination of size and shape fluctuations of the self-organized QDs cause the excited state spectrum for a given ground state transition energy to be still inhomogeneously broadened [25]. The FWHM of the excitation resonances might be taken as a measure for the shape uniformity of the QDs.

Figure 13 depicts two PLE spectra of the 3.00ML VDA sample taken near the PL maximum as a function of the excess excitation energy $\Delta E$. The most intense excitation resonances appear at energies of \( \sim 75, \sim 160, \) and \( \sim 240\text{meV} \) corresponding roughly to the excited state transitions observed in inhomogeneously broadened high-density PL spectra (not

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**Fig. 12:** Contour plot of the PL intensity in the 3.00ML VDA sample as a function of the detection energy and the excess excitation energy $\Delta E=E_{\text{exc}}-E_{\text{det}}$. The intensity is given on a logarithmic scale.
shown). However, additional weaker resonances are resolved at ~22, ~60, ~130, ~190, ...meV and lineshape fits to the PLE spectra suggest the presence of even more resonances. The excited state transition spectrum of the QDs is, therefore, denser than expected from inhomogeneously broadened spectra. These results give experimental evidence for the failure of a parabolic description of the electronic states of the QDs leading to a $\Delta n=0$ selection rule for dipole transitions as well as regularly spaced excited state transitions. Therefore, we compare the experimental results to numerical calculations based on the 8 band $\mathbf{k} \cdot \mathbf{p}$ approximation for pyramidal InAs/GaAs QDs with a base length between 10 and 20nm described in detail in Ref. [37]. The calculations indicate a variety of bound electron and hole states, whereby the substate splittings for the hole states are in the 10meV region and those of the electron states are in the 50meV region. Absorption spectra calculated based on the obtained wavefunctions show transitions between a variety electron and hole levels to have sufficient oscillator strength to be observed in experiments. The low symmetry of such strained self-organized QDs to cause a breakdown of the $\Delta n=0$ selection rule, although the most intense transitions have still matching 'quantum numbers' of the electron and hole wavefunctions [37]. Note, that in the strained pyramidal QDs n is no longer a good quantum number, and has been replaced for the classification of the wavefunction by the somewhat arbitrary number of nodes [37]. The calculated absorption strengths of the lowest energy transitions in a 17nm base-length pyramid is represented by bars in Fig. 13. The height of the bars corresponds to the relative transition probability. Figure 13 shows a good qualitative agreement between calculation and experiment supporting the 8 band $\mathbf{k} \cdot \mathbf{p}$ calculations and the assumed QD shape [53]. The excitation resonance at ~22meV corresponds to the transition between the electron ground state and the second excited hole state. At higher energies transitions involving excited electron states contribute to the spectrum. We remind, that in the 3.00ML sample the optically active QDs are grown on top of the smaller seed islands, which might influence their properties. However, for the comparatively thick (36ML) spacer electronic coupling is negligible [25] and, additionally, numerical calculations for such AQDPs indicate the strain-interaction to lead to blue-shift of the transition energies by a few meV, which is negligible for the presently available experimental results.

### III.5 Phonon-Assisted Exciton Recombination

Finally, we will discuss the exciton-LO-phonon coupling in the self-organized InAs/GaAs QDs, which is of fundamental interest for carrier relaxation processes as well as a sensitive test for the electron and hole wavefunctions, i.e. for the numerical calculations based on idealized QD shapes as discussed in the previous section. Recently, multi-LO-phonon progressions have been observed in PLE spectra of such QDs and unambiguously attributed

![Fig. 13: PLE spectra for the 3.00ML VDA sample for two different detection energies. Bars show the absorption strength of various electron and hole transitions calculated for a 17nm base-length pyramid [37]. The exciton ground state energy of the pyramid is 1.027eV.](image-url)
to the effects of the carrier dynamics following excited state absorption [24,30]. These results demonstrated inelastic phonon scattering to be the dominant carrier relaxation process at low carrier densities, but give no access to the actual exciton-LO-phonon coupling strength. However, for uniform InAs/GaAs QD samples with a ground state PL FWHM smaller than typical LO-phonon energies characteristic low-energy shoulders are observed for the ground state PL, see e.g. Figs. 2 and 14. These shoulders can be identified as phonon-assisted recombination processes giving direct access to the exciton-LO-phonon coupling strength [54].

The phonon-assisted exciton transitions are clearly resolved in site-selective PL and PLE spectra, circumventing the inhomogeneous broadening of the QD ensemble, Fig. 14(a). The pronounced modulation of the PLE efficiency (dotted spectrum) allows for the selective excitation of QDs with a ground state transition energy in resonance with the inhomogeneous PL maximum. Exciting the PLE resonance at 1.103eV, the QD PL peak at 1.027eV (dubbed zero phonon line (ZPL)) becomes narrower (FWHM=11meV) [55] and a peak (dubbed –LO) is clearly resolved in the region of the first low energy shoulder, having ~1.5% of the intensity of the ZPL. The -LO replica becomes a well-resolved separate peak exciting directly the ZPL. Gaussian fits of such higher resolved spectra yield an energy of 34.2meV for the phonon mode in good agreement with previous results for the QD LO phonon energy [24,30]. Figure 13(b) shows the dependence of integrated intensity of the +LO-phonon resonance observed in PLE spectra on the detection energy, proving the phonon-assisted transition to be resonant with the QD ground state transition. Two resonances centered at 1.027 and 0.993eV are revealed, which are resonant to the ground state transition and redshifted by one LO-phonon energy, respectively. The LO phonon is excited either in the generation or recombination of the ground state exciton, respectively. The PLE spectra of the ZPL and the –LO resonance (not shown) [54] show identical excitation resonances proving that in both cases the same QD sub-ensemble is probed as expected for a phonon-assisted transition.

The observation of the phonon-assisted optical transitions allows the determination of the Huang-Rhys parameter S for the polar exciton-LO-phonon coupling in the self-organized InAs/GaAs QDs. At low temperatures, the Huang-Rhys parameter S is given by the ratio of the intensities of the first LO-replica (-LO) and the ZPL [56], yielding S=0.014 for the 3.00ML VDA sample. The experimental results for the ground state transition energy and S are depicted in Fig. 15. Results from equivalent experiments (not shown) for smaller QDs in differently grown single-layer samples (dubbed GI and 3ML) are included, too [54].
The Huang-Rhys factors $S$ determined for the ground state exciton in the self-organized InAs/GaAs QDs are ~5 times larger than in bulk InAs ($S_{bulk} \approx 0.0033$) [57]. Surprisingly, exciton localization in the self-organized InAs/GaAs QDs enhances the polar exciton-LO-phonon interaction. The polar exciton-LO-phonon interaction ($S$), being proportional to the squared absolute value of the Fourier-transformed difference between the probability densities of the electron and hole [58], is expected to decrease with increasing confinement in highly symmetric QDs [59]. The polar exciton-LO-phonon coupling is a difference effect and, therefore, extremely sensitive to the particular electron and hole wavefunctions. For the strained, low-symmetry InAs/GaAs QDs the unique quantization and the piezoelectric potential lead to a separation of the electron and hole wavefunctions [37] and, therefore, an enhancement of the Exciton-LO-phonon coupling [54]. Consequently, the understanding of the experimental results must be based on realistic wavefunctions, i.e. 8 band $k \cdot p$ calculations including Coulomb interaction in the Hartree approximation [37], which reasonably well account for the experimentally observed ground state transition energy (open diamonds in Fig. 15(a)) and excited state spectrum (Fig. 13). The insets of Fig. 15(a) depict probability density isosurfaces ($p=65\%$) of the electron and hole ground states for $b=10.2\text{nm}$ and $b=20.4\text{nm}$. The electron wavefunction is predominantly s-like, whereas the hole wavefunction is partly p-like and, with increasing pyramid size, concentrates in the [1-10] corners of the pyramid as a result of the strain-induced piezoelectric potential.

The Huang-Rhys parameter $S$ is estimated within the adiabatic approximation for the interaction of the ground state exciton with bulk phonon modes, following the calculations of Nomura and Kobayashi (Eq. (8) in Ref. [58]) and using the above described wavefunctions. The results are depicted as open diamonds in Fig. 15(b). $S$ increases from 0.0020 to 0.027 by more than one order of magnitude doubling the pyramid baselength from 10.2 to 20.4nm. The piezoelectricity modifying the hole wavefunction [37] decisive for the pronounced enhancement of the coupling strength. Neglecting the piezoelectricity results in an ~70% reduction of the Huang-Rhys parameter $S$ (open dots in Fig. 15(b)). The good agreement between experimental (solid symbols) and calculated $S$ values indicates that the adiabatic approximation is able to explain the polar exciton-LO-phonon coupling in the coherent, defect-free InAs/GaAs QDs and supports the validity of the 8 band $k \cdot p$ calculations. The apparent lack of a clear size-dependence in the experimental data (solid symbols) results from the fact that the GI and 3ML samples have single QDs whereas the VDA sample contains the...
AQDPs. Numerical calculations for such AQDPs show the strain interaction between the small seed island and the optically active QD to cause mainly a reduction of the piezoelectric potential, leading to a significant decrease (~40%) of the Huang-Rhys parameter $S$ compared to an equivalent unpaired QD.

**IV. CONCLUSIONS**

We have reported on a thorough study of the optical properties of self-organized InAs/GaAs QDs using PL, PLE, and TRPL techniques as a function of temperature. The investigated samples contain asymmetric QD pairs allowing to control the size and improve the uniformity of the optically active QDs in the second layer. For the 36ML spacer used for most samples the electronic interaction of the QDs in such AQDPs is negligible, but only the larger one is optically active due to efficient intrapair energy transfer with a yield of ~1. Increasing the spacer thickness allows to suppress the energy transfer processes and, thus, to tune the carrier dynamics from the transfer to the recombination limited regime. The VDA samples enable the growth of a high density (~400µm$^{-2}$) of high-quality QDs providing room-temperature emission at 1.3µm, exciton localization with respect to the WL of ~430meV, and a PL FWHM of only 18meV. Room temperature exciton lifetimes of up to 150ps are estimated, which are determined by the thermal escape of the electrons. The PL intensity for nonresonant excitation is, however, quenched due to a decreasing capture efficiency with increasing temperature. The results suggest that AlGaAs diffusion barriers might drastically enhance the room temperature PL yield.

PLE spectra are shown to reveal the excited state transition spectrum for the investigated VDA samples, showing a much richer finestructure than expected from inhomogeneously broadened high-density PL spectra. A comparison to 8 band $k \cdot p$ calculations shows a breakdown of the $\Delta n=0$ selection rule and leads to a qualitative understanding of the excited state spectrum. The presence of the seed QD is shown to have only a negligible effect on the electronic properties of the optically active QDs in the second layer. Finally, phonon-assisted exciton recombination processes are identified indicating an enhanced polar exciton-LO-phonon interaction in the self-organized InAs/GaAs QDs. The experimental observations are well explained assuming adiabatic coupling to bulk-like phonon modes taking into account realistic wavefunctions. The particular quantum confinement and the piezoelectricity in the strained low-symmetry QDs result in the enhanced coupling strength. The presented results show that far-field spectroscopy on high-quality samples is able to provide a deep understanding of the electronic properties of self-organized InAs/GaAs QDs.

The variable deposition amount growth approach gives unprecedented control on the formation of self-organized QDs allowing to position, tune and shape these coherent defect-free QDs. In the present study we have used a self-organized seed layer. However, using artificially prepatterned stressors with a regular surface arrangement as seed layer might further improve this growth concept.

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REFERENCE

47. Y. P. Varshni, Physica 34, 149 (1967).
55. The weak shoulder at 1.044eV results from smaller QDs excited via a different excited state transition.
57. The Huang-Rhys factor of the bulk InAs exciton is calculated using Eq. (A4) in Ref. [58].