Assessing Carrier Recombination Processes in Type-II SiGe/Si(001) Quantum Dots

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In this work, it is shown how different carrier recombination paths significantly broaden the photoluminescence (PL) emission bandwidth observed in type-II self-assembled SiGe/Si(001) quantum dots (QDs). QDs grown by molecular beam epitaxy with very homogeneous size distribution, onion-shaped composition profile, and Si capping layer thicknesses varying from 0 to 1100 nm are utilized to assess the optical carrier-recombination paths. By using high-energy photons for PL excitation, electron-hole pairs can be selectively generated either above or below the QD layer and, thus, clearly access two radiative carrier recombination channels. Fitting the charge carrier capture-, loss- and recombination-dynamics to PL time-decay curves measured for different experimental configurations allows to obtain quantitative information of carrier capture-, excitonic-emission-, and Auger-recombination rates in this type-II nano-system.

1. Introduction

Over the last years, great efforts were made to obtain efficient light-emission from group-IV nanostructures, such as quantum dots (QDs),[1–8] in order to develop low-cost optically active materials that are to be integrated into Si technology.[4,9,10] The well-known drawbacks of SiGe QDs as light emitters are the indirect band gap of Si and Ge and the weak electron binding. Improvements of the optical properties of SiGe QDs, for example, with respect to emission linewidth and intensity, were proposed and demonstrated by the use of site-controlled QDs,[4,5,11–13] QDs embedded in strained layers,[14] or resonators such as photonic crystal cavities (PhC) or microdisks.[15–17] Recently, we demonstrated that introducing single defects by the implantation of heavy ions into the QDs can overcome the indirect nature of their radiative transitions,[18–21] leading to optically pumped lasing from microdisk cavities[19] containing such defect-enhanced quantum dots (DEQDs) as gain material. In addition, light emitting diodes based on DEQDs with efficient electrical injection of charge carriers were shown.[21]

Nevertheless, for a further development of Ge/Si and DEQD light sources, a detailed understanding of the carrier recombination paths in crystalline SiGe QDs is still necessary. This knowledge will also be crucial for the design of photonic resonators and especially for further developments toward quantum optics based on SiGe nanostructures.

The typical photoluminescence emission (PL) of randomly nucleated Ge/Si QDs is spectrally very broad[11,22–26] and can to some extent be narrowed by using site-controlled QDs on patterned substrates.[5,11–13,27] The PL emission from a single SiGe QD[27] grown on a pit-patterned substrate with wide pit period shows an inhomogeneous linewidth of about 16 meV even for the lowest measurable excitation powers. This is much broader than the lifetime-limited emission linewidth, which is to be expected in the µeV range, considering reported radiative lifetimes for SiGe.[28] Different interpretations of the broad PL linewidth of SiGe QDs include: i) size inhomogeneity of the QDs,[22–24] ii) compositional inhomogeneity between different QDs in an ensemble,[15] iii) state filling effects,[12] iv) bi-exciton formation at higher excitation intensities,[29] v) existence of a low-energy phonon replica,[30–32] vi) photo-induced band-bending effects,[23,24,33] vii) spectral diffusion[27] and fast dephasing.[34]

In this work, we demonstrate that energetically nondegenerate electron-hole (e-h) recombination paths[35–37] in the self-assembled QDs significantly broaden the QD PL emission, as proposed by Brehm et al.[38] To reveal those paths, we have grown by molecular beam epitaxy (MBE) on Si(001) substrates tailored samples with very homogeneous SiGe QDs that were subsequently capped by a crystalline Si layer with a thickness...
(tcap) that monotonously varied from 0 to 1100 nm across the substrate. The variation of tcap allows us to generate the majority of the e-h pairs either below (tcap < 1/α) or above (tcap > 1/α) the QD layer, depending on the ratio between tcap and the absorption length 1/α of the PL excitation laser radiation in Si. Here, α denotes the absorption coefficient of Si at the excitation laser wavelength. To the well-known different strain status of the Si matrix directly above the QDs' apex (tensilely strained Si, Δz-valleys) and at the periphery of the QDs' base (compressively strained Si, Δxy-valleys), different conduction band valleys form the local ground states for electrons. Their relative occupation depends on the location of maximum e-h pair generation. Depending on tcap at the position of the excitation laser spot, it is thus possible to select different excitation recombination channels, namely either Δz-HH or Δxy-HH transitions. We compare the optical transition energies of those two recombination paths to 3D band structure calculations of QDs with realistic 3D SiGe composition profiles. Our results shed new light on our basic understanding of carrier recombination paths, recombination dynamics, and Auger recombination mechanisms in epitaxial QDs with type-II band alignment.

2. Experimental Section

The growth of the samples was carried out on high-resistivity (>1000 Ωcm) Si(001) substrates in a Riber Siva 45 solid source molecular beam epitaxy (MBE) facility. After in situ oxide desorption at 950 °C for 20 min, we grew a 45 nm thick Si buffer layer at a growth rate of 0.6 Å s⁻¹ and at a growth temperature that was ramped up from 550 to 750 °C. Hereafter, seven monolayers (ML) of Ge were deposited at 750 °C and at a growth rate of 0.05 Å s⁻¹. We used this rather high Ge growth temperature to provide high morphological uniformity of the QDs, as explained in detail in Section 3.2. Before the growth of a Si capping layer at 350 °C, we inserted a manual shutter about 10 mm beneath the substrate, covering a part of the substrate to avoid the subsequent deposition of Si on a selected area of the sample. The Si capping layer with a thickness tcap of 1100 nm was then grown at a temperature ramped up from 350 to 500 °C to avoid detrimental Si intermixing with the thin Ge WL and the larger SiGe QDs.

By inserting the manual shutter, we obtained regions of uncapped Ge QDs, QDs embedded in an 1100 nm thick Si matrix, and, in the half-shadow region of the shutter, QDs buried under a Si cap with increasing thickness in the range between 0 and 1100 nm over an approximately 1.2 mm wide transition region (Figure 1a). For a complementary experiment, we processed quadratic mesas (length: 22 µm, depth: 2 µm) on the sample area with tcap = 1100 nm by inductively coupled plasma etching (Figure 1b).

After growth, the uncapped surfaces of the samples were characterized ex situ using a Digital Instruments Dimension 3100 atomic force microscope (AFM). For PL excitation, we used diode lasers operating at 442 and 657 nm as well as an Ar-ion laser at 457 nm. A microscope objective with a numerical aperture of 0.7 was used both for laser focusing and for collecting the PL signal from the sample. A continuous flow cryostat allowed for sample cooling down to 10 K. The laser spot diameter on the sample was ∼2 µm wide. The PL signal was dispersed by a grating spectrometer and recorded using a nitrogen-cooled InGaAs line detector. For time-resolved measurements, we excited the samples by a pulsed laser (wavelength λ = 442 nm), with a pulse width of ∼200 ps and an average optical power ranging from 240 to 2900 nW in a laser spot of ∼2 µm diameter at a repetition rate of 1 MHz. The time-delay between excitation pulse and PL photon detection was measured by a superconducting single photon detector (SSPD) from Scontel at 1.8 K connected to a PicQuant time correlator. The time jitter of the SSPD was ∼30 ps so that the time resolution of the setup used in this work was limited by the laser pulse width.

3. Results and Discussion

3.1. Morphological QD Properties

Figure 2 displays the morphological structure of the QDs, as measured by AFM, in a height mode image (Figure 2a) and in a color-coded surface angle image (SAI) (Figure 2b). From the evaluation of two large-area images of 5 × 5 µm² size (histograms in Figure 2c,d), we find that 98.8% of the QDs are of dome-shape with an average height of 30.6 ± 1.8 nm and a respective volume of 2.0
fining potentials for holes that are distinctly different\cite{12,44} from “potential wells” with flat band offsets. In some cases, Ge-rich cores are found in QDs leading to strong 0D carrier confinement despite their 100–200 nm wide lateral extension.\cite{12,48}

In self-assembled QDs grown by MBE at temperatures below \(\approx 700 \, ^\circ\text{C}\), the Ge content was found to be low at the base and increasing toward the apex of the QDs.\cite{14,49–53} For QDs grown by chemical vapor deposition (CVD), distinctly different composition profiles were found, exhibiting a Si-rich QD core and a Ge-rich shell at the surface of the QD (“onion shape”).\cite{55,56} This “onion shape” composition profiles derive from near-equilibrium processes and enhanced intra-QD diffusion, usually present during CVD-growth of QDs already for growth temperatures of \(600 \, ^\circ\text{C}\).\cite{55,56} Composition profiles with Ge-rich cores at the apex of the QD and a rather linear Ge gradient in growth direction are typically found in MBE grown structures and originate from the nonequilibrium nature of MBE growth.\cite{56} Here, we stress that the MBE growth conditions chosen in this work for QD growth are closer to thermal equilibrium, and result also in onion shape composition profiles, supporting the results found by Georgiou et al.\cite{56}

To assess the 3D SiGe composition profile in the QDs, we used the nano-tomography technique based on selective wet etching developed by Rastelli et al.\cite{49}

Figure 3a depicts vertical cross sections of the Ge content across four different QDs passing through the QD-centers along the \{110\}-direction. Despite the rather uniform Ge distribution, we observe a rather homogeneous, Ge-lean core with a Ge content of about 35\% (green colour), and, toward the QD surface, an increase in Ge concentration to \(\approx 55\%\) (red color). Notably, the Ge content at the apex of the QDs is slightly lower (45–50\%) than at the side facets. The “onion-shape” of the Ge composition in the QDs is also evident in the horizontal cross sections through the QDs at heights of 2 nm (Figure 3b), 6 nm (Figure 3c), and 20 nm (Figure 3d), respectively, with respect to the level of the WL surface. In Figure 3e, we plot the average Ge content of the QDs for the areas shown in Figure 3b–d along the growth direction as a function of their height. The average Ge content increases from \(\approx 38\%\) at the QDs base to \(\approx 47\%\) at their apex.

Based on the AFM and nanotomography results, we performed QD energy level calculations for heavy holes, light holes, and electrons using the nextnano++ simulation tool.\cite{57,58} The nextnano++ calculations are based on an effective mass envelope function approach, taking fully into account the strain tensor field in both the QD and the Si matrix, as well as the multi-valley nature of the conduction and valence bands. The relevant material parameters for Si and Ge used in the calculations are given by Klenovský et al. and Brehm et al.\cite{29,53} In Figure 3f, the cone-shaped QD is plotted in grey, the electron- and hole-distributions are indicated by bubble-like iso-surfaces, outside which the probability density to find a carrier has decayed to less than 10\% of the maximum probability density of the respective state. The heavy-hole (HH) states within the QD are depicted in green while the \(\Delta_e\) electron ground state in the tensile strained Si above and the \(\Delta_{ox}\) electron ground states in the compressively strained Si at the periphery of the QD are plotted as red and blue iso-surfaces, respectively. Due to the aforementioned SiGe composition profile in the QDs, the HH states are spread across the QD, leading to energy-minima both at the QD-apex and base

\[ x = 10^3 \pm 2.2 \times 10^3 \, \text{nm}^2. \]  
Evidently, the domes have a very narrow size distribution and only a few pyramids\cite{47} are present.

### 3.2. Chemical Properties of the QDs and Band-Structure Calculations

The Ge composition in QDs is either determined by SiGe intermixing effects between the Ge epilayer and the underlying Si substrate\cite{44,45,48–53} or by the Si cap if the growth temperature of the Si capping layer is too high.\cite{44,45} In turn, the Ge distribution within a QD and its influence on the strain status of the Si matrix determines the hole and electron localization as well as the energy difference between electron and hole states, and, thus, the carrier recombination paths and optical transition energies in hetero-epitaxially formed wetting layers (WLs)\cite{44} and QDs.\cite{35}

Homogeneous SiGe intermixing within the whole volume of the QDs is, however, not found in MBE-grown samples. Inhomogeneous Ge composition, that is, Ge-lean along with Ge-rich regions critically change the local band offsets\cite{54} leading to constant fine tuning potentials for holes that are distinctly different\cite{12,44} from “potential wells” with flat band offsets. In some cases, Ge-rich cores are found in QDs leading to strong 0D carrier confinement despite their 100–200 nm wide lateral extension.\cite{12,48}
energetically separated only by a few meV. Due to increased strain, the Δx-electron valley in the tensile strained Si matrix above the QD (red color) represents the global energy minimum for electrons, albeit the slightly lower Ge content at the QD’s apex as compared to the sidewalls. The calculated ground state transition energies from Δx-HH and Δy-HH are 784 and 837 meV, respectively. The corresponding average joint density of states for optical transitions are 0.25/meV and 0.8/meV, respectively. The corresponding average joint density of states have decayed below 10% of their maximum values. The QD is indicated as a light grey cone.

3.3. PL Spectroscopy on QDs in Mesa Structures

For both, the sample with the graded thickness of the capping layer and the sample with the mesa structures, electron-hole pairs can be excited dominantly either below (α-tcap ≫ 1) or above (α-tcap ≪ 1) the QD layer, depending on the magnitude of α-tcap at the position of the excitation laser spot. Assuming the wetting layer forming a barrier against carrier diffusion from the capping layer to the substrate and vice versa, this allows us to enhance either the Δy-HH or the Δx-HH optical recombination path and to obtain insights into the dynamics of these paths for our single layer type-II QDs. The assumption of a diffusion barrier is made ad hoc here. However, all the following results of this work are interpreted based on this assumption and no contradictions to it were found in our results.

First, we measure the PL response as a function of the laser excitation spot position on the sample with mesa configuration. Figure 1b shows a schematic representation of the experimental configurations. While for both configurations, our detection spot is on the mesa, we excite the sample either on the mesa (“on-mesa”) or 20 µm away from the mesa (“off-mesa”). Due to geometrical reasons, the carriers cannot be as efficiently trapped by the QDs for “off-mesa” as for “on-mesa” laser excitation. In Figure 4a,b, we compare the shape of PL spectra measured for the two experimental configurations excited with a laser wavelength of 457 nm. The continuous-wave (cw) excitation intensities were adjusted so that the integrated PL intensities were equal for both experimental configurations (50 µW for “on-mesa” and 1.2 mW for “off-mesa”). In this way, we avoid an influence of unequal numbers of e-h pairs occupying the QDs (filling effects) on their spectral PL shape in the two configurations. Distinctly different PL-spectra are observed for excitation “off-mesa” and “on-mesa”.

For the former (Figure 4a), we observe a pronounced splitting of the PL signal commonly assigned to a no-phonon assisted (NP) peak and a transversal optical phonon-assisted (TO) transition.[30] For the latter, the PL peak related to the QDs is rather broad and unstructured.

To extract different contributions of the two radiative recombination paths (Δx-HH and Δy-HH), we fitted the spectra with two doublets of Gaussian functions, each consisting of an NP and a TO-peak[30] for both possible recombination paths.

For the “off-mesa” configuration, the e-h-pairs are generated exclusively below the QDs, that is, the optical transitions are of type Δy-HH. Thus we performed an initial fit for the “off-mesa” configuration using a doublet of Gaussian functions, that is

\[ P_{L_{xy}} = A_{xy}^{NP} \cdot e^{-(E_{xy}^{NP} - \sigma_{NP})^2 / (2 \sigma_{NP}^2)} + A_{xy}^{TO} \cdot e^{-(E_{xy}^{TO} - \sigma_{TO})^2 / (2 \sigma_{TO}^2)} \] (1)

where for the fitted NP and TO-phonon contributions A \( A_{xy}^{NP} \) and \( A_{xy}^{TO} \) denotes the peak amplitude, \( \sigma \) \( \sigma_{xy}^{NP} \) and \( \sigma_{xy}^{TO} \) the peak width, and E \( E_{xy}^{NP} \) and E \( E_{xy}^{TO} \) their spectral position. The resulting fit is shown in Figure 4a by the blue and black (sum) lines. The spectral positions of \( E_{xy}^{NP} \) and \( E_{xy}^{TO} \) were found to be \( 0.8588 \pm 5 \times 10^{-4} \) and \( 0.8155 \pm 1.1 \times 10^{-3} \) eV, respectively, leading to a phonon splitting of \( 4.3 \pm 1.2 \) meV.

For the configuration “on-mesa”, the situation is a bit more complex. While e-h pairs are dominantly generated above the QDs, a smaller fraction (about 7%) is also generated below, owed to the absorption coefficient in Si for the photons emitted by the excitation laser with \( \lambda = 457 \) nm \( (\alpha \approx 2.4 \times 10^4 \text{cm}^{-1}) \).[38,39] Hence, for fitting the spectrum recorded in the “on-mesa” configuration (grey spectrum in Figure 4b), the result of the above-described
Figure 4. Low temperature (10 K) PL-spectra of the QDs detected on the mesa for excitation a) “off-mesa” and b) “on-mesa”. The excitation power $P$ was chosen in such a way that the integrated PL intensities of the spectra obtained by excitation “on” and “off” the mesas are comparable. The black curves in (a) and (b) fit to the spectra using pairs of Gaussian functions, corresponding to NP and TO phonon-assisted transitions. Blue and red peaks correspond to $\Delta_{xy}$-HH and $\Delta_{z}$-HH, respectively. Insets schematically depict the experimental setup. The right inset in (a) represents an optical microscopy image of the experimental configuration “off” the mesa.

The two measurement configurations, “off-mesa” and “on-mesa” are different in terms of excitation conditions due to the large laser-spot-to-QD distance in the “off-mesa” configuration and the non-passivated surface areas created by reactive ion etching of the mesa. Therefore, a more detailed interpretation remains difficult. However, the presented data support the initial assumption that possible PL contributions in type-II Ge-on-Si QDs originate from both, $\Delta_{z}$-HH and $\Delta_{xy}$-HH transitions, where the ratio of the two contributions depends on the fraction of absorbed light below and above the QD-layer.

To clearly strengthen this point, in the following PL investigations performed on the sample area with varying $t_{\text{cap}}$ will be presented. In this way, it is possible to keep the laser excitation conditions constant and continuously vary the ratio of the number of e-h-pairs generated above and below the QD layer.

3.4. PL Spectroscopy on QDs with Monotonously Increasing Si Cap Thickness

For a systematic investigation of the influence of carrier generation above or below the QD layer on the QD PL emission, we employed the sample area with continuously increasing Si $t_{\text{cap}}$ from 0 to 1100 nm over a distance of about 1.2 mm (see the experimental configuration in Figure 1a).

In Figure 5a, the spectra recorded from a PL line-scan along the $t_{\text{cap}}$-gradient are plotted (grey color). Alongside this gradient, the QD-related PL emission shape and yield change significantly from a low-intensity, spectrally unstructured PL peak for large $t_{\text{cap}}$ to a strong PL peak accompanied by a clear low-energy shoulder for small $t_{\text{cap}}$. This is clearly consistent with the previously discussed results on the two mesa configurations, where “off-mesa” and “on-mesa” resemble small and maximum $t_{\text{cap}}$, respectively.

For $t_{\text{cap}} \leq 20$ nm and for $\lambda = 457$ nm, it can be assumed that all e-h pairs are generated below the QD layer in the Si substrate and...
the PL emission consists entirely of $\Delta_{xy}$-HH transitions, similarly to the “off-mesa” configuration. In analogy to the fitting of the mesa spectra, in an initial fitting step, a Gaussian doublet function accounting to the NP and TO-phonon transitions of the $\Delta_{xy}$-HH transition was fitted for a spectrum recorded at $t_{\text{cap}} = 20 \text{ nm}$. Note that for $t_{\text{cap}} = 2 \text{ nm}$, the QD-related PL is weak which might be related to leakage of the hole wave-functions to surface states of the Si capping layer from which the carriers can recombine non-radiatively. For $t_{\text{cap}} = 5$ and 10 nm, the high-energy shoulder of the QD-related PL is shifted to lower energies with respect to the PL observed for $t_{\text{cap}} \geq 20 \text{ nm}$ as indicated in Figure 5a by the superimposed PL spectra for $t_{\text{cap}} = 20 \text{ nm}$ shown by the broken lines. This shift is attributed to a larger strain present in the Si above the QD for capping layer thicknesses smaller than the strain decay length and renders these spectra nonrepresentative for those measured for $t_{\text{cap}} \geq 20 \text{ nm}$. The resulting energies $E_{\text{NP}}^{xy}$ and $E_{\text{TO}}^{xy}$ for $t_{\text{cap}} = 20 \text{ nm}$ were found to be $0.884 \pm 0.001$ and $0.831 \pm 0.002 \text{ eV}$, respectively. Subsequently, the spectrum for $t_{\text{cap}} = 1000 \text{ nm}$ was fitted by adding an additional doublet of Gaussian peaks accounting for the NP and TO-phonon transitions of the $\Delta_{z}$-HH transition ($\text{PL}_z$) to a fraction $f_{\text{xy}}$ of the $\Delta_{xy}$-HH transition found for $t_{\text{cap}} = 20 \text{ nm}$. We found that a fraction $f_{\text{xy}}$ of about $7.3 \pm 0.5\%$ fits the series of spectra well. The spectra for all other $t_{\text{cap}}$ were fitted using a linear combination of the fitting curves for $\text{PL}_x$ and $\text{PL}_z$, that is, $\text{PL}(t_{\text{cap}}) = f_2(t_{\text{cap}})\text{PL}_x + f_3(t_{\text{cap}})\text{PL}_z$. The results of the fitting procedure are shown in Figure 5a where the Gaussian functions related to $\Delta_{xy}$-HH and $\Delta_{z}$-HH transitions are shown in blue and red.
respectively. The sum of both, depicted by the black lines, is in excellent agreement with the measured spectra for a wide range of $t_{\text{cap}}$.

In Figure 5b, the fraction of the integrated QD PL emission originating from $\Delta_{\text{xy}}$-HH and $\Delta_{\text{z}}$-HH transitions, as determined by the fitting procedure, are plotted over $t_{\text{cap}}$ by blue and red diamonds, respectively. Additionally, the fraction of e-h pairs generated below (blue thick lines) and above (red thick lines) the QD layer was calculated considering the absorption coefficient in Si (for 10 K) for laser excitation at $\lambda = 457 \text{ nm}$. As in the case of the mesa configuration (Section 3.3), the similar behavior of the layer absorption. Vice versa, and consistent with the slight 0.862 Si-bulk PL (PL Si), and the WL-PL (PL WL) contributions. Since the $\lambda = 675 \text{ nm}$, $\alpha$ is about an order of magnitude smaller than for $\lambda = 457 \text{ nm}$. Therefore, for $\lambda = 675 \text{ nm}$, the majority of the e-h pairs is generated below the QD layer, independently of $t_{\text{cap}}$ (Figure 6b). Thus, not surprisingly, the QD PL emission spectra are very similar with respect to their shape and a clear double peak structure—a sign for dominant $\Delta_{\text{y}}$-HH recombination—can be found even for $t_{\text{cap}} = 1000 \text{ nm}$ (Figure 6a). In Figure 6b, the fraction of the integrated QD PL emission originating from $\Delta_{\text{xy}}$-HH and $\Delta_{\text{z}}$-HH transitions, as determined by the fitting procedure, are plotted over $t_{\text{cap}}$ by blue and red diamonds, respectively. Additionally, the fraction of e-h pairs generated below (blue thick lines) and above (red thick lines) the QD layer was calculated considering the absorption coefficient in Si (for 10 K) for the laser excitation at $\lambda = 657 \text{ nm}$.

The agreement in Figure 6b suggests that the deviation of the expected values and data points extracted from the measurements with $\lambda = 457 \text{ nm}$ (Figure 5b) is not due to positioning errors in $t_{\text{cap}}$ during the PL measurements but rather influenced by loss mechanisms in the Si capping layer and the sample surface. Because of the low absorption in the Si capping layer, those additional losses have an only minor impact on the integrated QD PL (Figure 6c).

3.5. Time-Resolved PL Spectroscopy

From the cw-PL spectroscopy experiments described in Sections 3.3 and 3.4, we concluded that different electron-hole recombination paths broaden the PL emission of Ge/Si QDs. Time-resolved PL spectroscopy shall now provide details of the respective recombination rates involved.

When an ensemble of QDs or, similarly, when a single QD is repeatedly excited, the PL yield is dependent on the specific distribution of exciton numbers as pointed out by Julsgaard et al.\([2]\) If $p_m$ is the probability of finding $m$ excitons in the QD, the rate $\frac{\partial p_m}{\partial t}$ at which this probability changes can be written as:\([2]\)

$$\frac{\partial p_m}{\partial t} = \Gamma_{\Delta} \left[ p_{m+1}(m+1)^2 - p_m m^2 \right] + \frac{1}{4} \Gamma_{\Delta} \left[ p_{m+1}(m+1)^2 m - p_m m^2 (m-1) \right] + \Gamma_c \left[ p_{m-1} - p_m \right] n_f(t)$$

(2)

The first term on the right-hand side of Equation (2) describes e-h recombination processes which occur with a single-exciton recombination rate $\Gamma_{\Delta}$ that is enhanced by the combinatorial factor $m^2$, counting the number of possible pair recombination paths in the presence of $m$ electrons and $m$ holes. Both a decay of the $m$-pair occupation (into an $m-1$ pair occupation) as well as a build-up (from an $m+1$ pair occupation) are accounted for. In exact analogy, the second term of Equation (2)’s right-hand describes the dynamics of the exciton occupation probability $p_m$ due to Auger recombination occurring at a rate $\Gamma_{\Delta}$ combinatorically

$$\frac{\partial p_m}{\partial t} = \Gamma_{\Delta} \left[ p_{m+1}(m+1)^2 - p_m m^2 \right] + \frac{1}{4} \Gamma_{\Delta} \left[ p_{m+1}(m+1)^2 m - p_m m^2 (m-1) \right] + \Gamma_c \left[ p_{m-1} - p_m \right] n_f(t)$$

The recorded spectra together with the results of the fitting procedure conducted as described above are shown in Figure 6a. Also here, the spectra with $t_{\text{cap}} < 20 \text{ nm}$ were excluded from the fits, because of the variations of the QD strain for small values of $t_{\text{cap}}$, as discussed in more detail in the context of Figure 5a. For $\lambda = 675 \text{ nm}$, $\alpha$ is about an order of magnitude smaller than for $\lambda = 457 \text{ nm}$. Therefore, for $\lambda = 675 \text{ nm}$, the majority of the e-h pairs is generated below the QD layer, independently of $t_{\text{cap}}$ (Figure 6b). Thus, not surprisingly, the QD PL emission spectra are very similar with respect to their shape and a clear double peak structure—a sign for dominant $\Delta_{\text{y}}$-HH recombination—can be found even for $t_{\text{cap}} = 1000 \text{ nm}$ (Figure 6a). In Figure 6b, the fraction of the integrated QD PL emission originating from $\Delta_{\text{xy}}$-HH and $\Delta_{\text{z}}$-HH transitions, as determined by the fitting procedure, are plotted over $t_{\text{cap}}$ by blue and red diamonds, respectively. Additionally, the fraction of e-h pairs generated below (blue thick lines) and above (red thick lines) the QD layer was calculated considering the absorption coefficient in Si (for 10 K) for the laser excitation at $\lambda = 657 \text{ nm}$. The agreement in Figure 6b suggests that the deviation of the expected values and data points extracted from the measurements with $\lambda = 457 \text{ nm}$ (Figure 5b) is not due to positioning errors in $t_{\text{cap}}$ during the PL measurements but rather influenced by loss mechanisms in the Si capping layer and the sample surface. Because of the low absorption in the Si capping layer, those additional losses have an only minor impact on the integrated QD PL (Figure 6c).
enhanced by the factor \( m^2(m - 1)/2 \). In agreement with refs. [2,61], by using the combinatorial enhancement factors we neglect selection rules restricting the number of decay channels as a consequence of the orbital wave-function symmetries [62].

The inhomogeneous term in Equation (2) describes the nonresonant excitation of the QD. Here, \( n_\gamma(t) \) is the average number of free excitons per QD excited by a pump laser in the Si matrix surrounding the QDs, and \( \Gamma_\gamma \) is the average rate at which an exciton is captured by the QD. It can be shown, that in the limit of excitation pulses much shorter than any decay processes described by Equation (2) the effect of the inhomogeneous part of Equation (2) can be transformed into initial Poissonian distributions \( p_{m_{\Delta x y, \Delta z}} \) for excitons involving \( \Delta x y \) and \( \Delta z \) electrons according to ref. [63]

\[
p_{m_{\Delta x y, \Delta z}}(0) = \frac{1}{m!} e^{-n_{\Delta x y, \Delta z}} (n_{\Delta x y, \Delta z})^m
\]

where \( n_{\Delta x y} \) and \( n_{\Delta z} \) denote the average number of excitons captured into the \( \Delta x y \) and \( \Delta z \) QD states, respectively. From the temporal evolution of all \( p_m \), the average PL intensity \( I(t) \) that is measured by a detector in a PL setup with detection efficiency \( \eta \) can be calculated by weighting the detected radiative fraction \( \xi = \eta \Gamma_{\Delta} / \Gamma_\Delta \) of the e-h pair recombination in the presence of \( n \) e-h pairs by the probability \( p_m \) and summing over all \( m \), that is

\[
I(t) = \xi \Gamma_{\Delta} \sum_{m=0}^{m_{\text{max}}} p_m(t) m^2
\]

From the homogeneous part of Equations (2) and (3), it is clear that a mono-exponential PL decay is only obtained if exactly one e-h pair is present in the dot, that is, \( p_m = 0 \) for all \( m > 1 \). In all other cases of finite QD occupancy, multi-exponential PL traces with...
fast initial decay result also in cases where Auger processes can be neglected and the transition between multi- and single-exciton regimes is naturally described by Equation (2). Please note, that due to the nonlinear recombination model, the QD recombination rates depend on $n_{\Delta z}$ and $n_{\Delta y}$. Thus, it has to be checked after fitting the decay model to the experimental data, whether the assumed separation of time scales resulting in the Poissonian initial condition is met (see Supporting Information).

As verified by the cw-PL experiments discussed in the previous paragraphs, the sample design in this work allows us to control the ratios of the PL contributions originating from $\Delta_{xy}$ and $\Delta_{z}$-electron valleys. In the following, investigations on the PL dynamics of this system will be presented leading to quantitative conclusions on radiative and Auger-driven recombination rates for the excitons in the two different types of conduction band valleys relevant for this type-II QD system.

In Figure 7a,b, low temperature (10K) time-resolved PL measurements of the sample area with varying $t_{\text{cap}}$ are shown for two different laser pulse energies (average power $P$ of 320 and 2700 nW on a laser spot of $\approx 2 \mu m$ diameter and 1 MHz repetition rate). Only a Si filter at room temperature is used to block the Si PL emission and the laser photons so that all optical QD transients are observable and the transients shown in Figure 7. For lower $P$ (Figure 7a), the shape of the decay curves strongly depends on $t_{\text{cap}}$. For large $t_{\text{cap}}$, a fast initial PL decay can be observed which is gradually slowing down for thinner $t_{\text{cap}}$, where the PL dynamics almost exhibits mono-exponential behavior ($t_{\text{cap}} = 5 \text{ nm}$).

In contrast, for $P = 2700 \text{ nW}$, even for very thin $t_{\text{cap}}$, a fast initial decay can be observed and the time traces show similar properties for all $t_{\text{cap}}$, as plotted in Figure 7b.

The observed decay behavior can be attributed to differences in the $\Delta_{xy}$-HH and $\Delta_{z}$-HH exciton population dynamics as shown below. The PL decay curves are modeled based on the rate equations described above with the relevant decay constants and initial valley occupancies schematically depicted in Figure 7c. Depending on $t_{\text{cap}}$, a single laser pulse generates e-h pairs above (below) the QD layer. Per QD, an average number $n_{\Delta z} (n_{\Delta y})$ of them is captured as $\Delta_z (\Delta_y)$ excitons. To eliminate the dependence of the fitting parameters $n_{\Delta z}$ and $n_{\Delta y}$ on $t_{\text{cap}}$, we replace them by the global parameters $n_{\Delta z}^{\infty}$, $n_{\Delta y}^{\infty}$ via the ansatz $n_{\Delta z} = n_{\Delta z}^{\infty} \cdot \exp(-t_{\text{cap}}/\tau_{\Delta z})$ and $n_{\Delta y} = n_{\Delta y}^{\infty} \cdot \exp(-t_{\text{cap}}/\tau_{\Delta y})$, respectively. In this ad-hoc ansatz, we neglect the small deviations of the experimental PL yield from the calculated absorption profiles shown in Figure 5b. As discussed in Section 3.4, effects of carrier diffusion to and recombinaction at the surface are virtually the same for all $t_{\text{cap}}$ as a result of carrier diffusion lengths much larger than all $t_{\text{cap}}$. Therefore, these effects are contained in the parameters $n_{\Delta z}^{\infty}$, $n_{\Delta y}^{\infty}$ and thus are combined with bulk recombination effects.

The exciton decay is governed by the pair- and Auger-recombination rates $\Gamma_{\Delta z}$ and $\Gamma_{\Delta y}$ ($\Gamma_{\Delta z}$ and $\Gamma_{\Delta y}$), respectively. In Figure 7a,b, PL decay curves calculated according to Equation (3) from the simulated decay of the occupation probabilities for both $\Delta_{xy}$-HH and $\Delta_{z}$-HH excitons are indicated by blue and red lines, respectively. For each exciton type $i \in \{xy, z\}$, the parameters for the exciton population-dynamics $n_{\Delta i}^{\infty}$, $\Gamma_{\Delta i}$, $\Gamma_{\Delta i}^{-1}$, were treated as fitting parameters. In addition, an average efficiency factor $\xi$ common to both types of excitons as defined in Equation (3) was used for fitting. In a first fitting step, one set of fitting parameters $(n_{\Delta z}^{\infty}, \Gamma_{\Delta z}, \Gamma_{\Delta z}^{-1}, i \in \{xy, z\})$ was used to account for all decay curves recorded under low laser excitation. Only $\xi$ was
Table 1. Resulting set of values from fitting the PL decay curves at sample positions with different $t_{\text{cap}}$ for $P = 320$ nW at $\lambda = 442$ nm; as consistency check, for $P = 2700$ nW, the same decay constants as fitted for $P = 320$ nW were used in the simulations.

| $\Gamma_{\text{xy}}$ | $\Gamma_{\text{z}}$ | $\Gamma_{\text{xy}}$ [ns] | $\Gamma_{\text{z}}$ [ns] | $\Gamma_{\Delta_{\text{xy}}}$ [ns] | $\Gamma_{\Delta_{\text{z}}}$ [ns] |
|---------------------|---------------------|------------------------|------------------------|------------------------|------------------------|
| 320 nW              |                     |                        |                        |                        |                        |
| 4.05                | 0.73                | 0.0103                 | 0.0055                 | 0.1263                 | 0.0115                 |
| $\pm 0.34$          | $\pm 0.18$          | $\pm 0.0016$           | $\pm 0.0004$           | $\pm 0.0270$           | $\pm 0.0055$           |
| $<\xi>$ = $2.91 \times 10^{-3}$ | $1.90 \times 10^{-3}$ |

2700 nW

| 7.07                | 13.96               | $\pm 0.34$             | $\pm 0.18$             | $\pm 0.0270$           | $\pm 0.0055$           |
| $<\xi>$ = $2.94 \times 10^{-3}$ | $1.19 \times 10^{-3}$ |

varied independently to obtain good agreement with the decay curves measured for different $t_{\text{cap}}$. We want to point out that both the pair- and the Auger decay channels described by the rates $\Gamma_{\text{xy}}$ and $\Gamma_{\text{z}}$, respectively, where $i \in \{\text{xy}, \text{z}\}$, result in fast initial decays in the presence of multi-exciton excitations. However, at later times, at which the exciton population has decayed to the last exciton in the QD, the decay becomes mono-exponential with a decay rate of $\Gamma_{\text{xy}}$ and independent of $\Gamma_{\text{z}}$. This situation is described by the $m = 1$ terms in Equation (2). Thus, in order to determine $\Gamma_{\text{xy}}$ and $\Gamma_{\text{z}}$ by a fitting routine, it is essential that the experimental decay curve contains a section of mono-exponential decay with an integrated intensity not too small as compared to the integrated intensity of the fast, initial decay, so that in the fitting procedure the total residual to be minimized contains a significant contribution of the mono-exponential section of the decay curve. As a consequence, in this work, the decay curves measured at low excitation power ($P = 320$ nW) shown in Figure 7a were used for fitting the decay constants, since in these traces sections with mono-exponential decay are clearly evident (see Figure 7a). The resulting values for $\Gamma_{\text{xy}}$, $\Gamma_{\text{z}}$, (i $\in \{\text{xy}, \text{z}\}$) are listed in Table 1. To demonstrate their significance, the experimental decay traces shown in Figure 7b for a larger pump power of $P = 2700$ nW were simulated with these decay constants and only the parameters $n_{\text{xy}}^\infty$, $n_{\text{z}}^\infty$, and $\xi$, were used for fitting. The resulting simulated PL decay curves are shown in Figure 7a,b by the black lines with contributions of the $\Delta_{\text{xy}}$ ($\Delta_{\text{z}}$) excitons indicated by the blue (red) lines. Excellent agreement with the experimental data shown in grey for both values of the excitation power, demonstrating the significance of the extracted decay constants within our model assumptions.

Table 1 summarizes all parameter values obtained by fitting as described above. The values $<\xi>$ denote the mean values of $\xi$ obtained for different $t_{\text{cap}}$. Within their error bars, we obtain identical values of $<\xi>$ for low- and high-power excitation, further indicating that our model adequately describes the exciton dynamics in the QDs of this work for both excitation regimes. Noticeably, the rates related to $\Delta_{\text{xy}}$-HH excitons are much higher than the corresponding rates connected to $\Delta_{\text{z}}$-HH excitons. For the pair recombination rates, $\Delta_{\text{xy}}$-HH excitons recombine approximately twice as fast as $\Delta_{\text{z}}$-HH ones. We obtain an even larger respective ratio of approximately 10 for the Auger rates. We ascribe these findings tentatively to the larger overlap as well as to the much tighter confinement of the single particle electron/hole wave-functions involved in the $\Delta_{\text{xy}}$-HH excitons as compared to the ones of the $\Delta_{\text{z}}$-HH excitons (see insets of Figure 4 for a sketch of the respective wave-functions). For 320 nW excitation, $\Delta_{\text{xy}}$-HH QD excitons are generated approximately 5.5 times more efficiently than $\Delta_{\text{z}}$-HH ones as indicated by the ratio of $n_{\text{xy}}^\infty/n_{\text{z}}^\infty$ listed in Table 1 for that power.

The interpretation of the data compiled in Table 1 in terms of PL photon efficiency per absorbed pump photon is not as straightforward as it might seem. It follows, for example, from our model, that for the lower pump power reported in Table 1 (320 nW) more $\Delta_{\text{xy}}$ than $\Delta_{\text{z}}$ PL photons per absorbed pump photons are emitted, despite the larger Auger loss rate derived for $\Delta_{\text{z}}$ excitons. This finding is due to the fact that the Auger loss becomes insignificant for average exciton numbers $<n>$ $<1$ together with our result that the $\Delta_{\text{xy}}$ states capture e-h pairs more efficiently than the $\Delta_{\text{z}}$ states ($\Gamma_{\text{xy}} > \Gamma_{\text{z}}$) and our assumption of equal $\xi$ for both types of excitons.

These findings become reversed at large pump powers. In this case, the average number of excitons becomes large for both types of excitons and the number of Auger processes occurring per pair recombination event thus becomes decisive in comparing efficiencies per absorbed pump photon. Based on the parameters listed in Table 1 for a pump power of 2700 n W, a $\Delta_{\text{xy}}$ pair recombination efficiency per absorbed pump photon smaller than the respective value for the $\Delta_{\text{z}}$ excitons is obtained within our model for $t_{\text{cap}} \alpha_{\text{Si}} > 0.25$.

Note that the experimental data shown in Figures 5b and 6b were obtained under cw-pumping excitation. Under steady-state conditions, a large number of excitons is occupying the QD states and, similar to the case of large pump power, the Auger recombination rates determine the observed PL efficiency per absorbed pump photon, rendering the $\Delta_{\text{xy}}$ PL more efficient than the $\Delta_{\text{z}}$ PL.

We want to emphasize that the conclusions of the discussion of the relative efficiencies of $\Delta_{\text{xy}}$ and $\Delta_{\text{z}}$ PL strongly depend on the energetic structure and the extension of the wave-functions of the QD states formed in the $\Delta_{\text{xy}}$ and $\Delta_{\text{z}}$ and HH energy minima in and around the QD. These are in turn depending on the QD’s Ge distribution as well as strain fields, which are specially designed to allow the experiments of this work.

4. Conclusion

In this work, we use tailored SiGe QD samples with onion-shaped composition profiles and various Si capping layer thickness from 0 to 1100 nm to investigate carrier recombination paths in epitaxial SiGe on Si quantum dots by selective e-h pair generation either above or below the QD layer. In addition to the well-known and documented $\Delta_{\text{xy}}$-HH related transitions, contributions from $\Delta_{\text{z}}$-HH transitions were also identified in this type of QDs. The QD PL fraction of the two contributions is directly related to the fractions of e-h pair generated in the capping layer and the substrate, confirming that the very thin ($\approx 3.2$ ML) type-II potential of the WL acts as an efficient barrier for electron-diffusion as assumed as prerequisite for interpreting our QD PL results. For low sample temperatures, the holes are trapped in the WL or the QD.
and cannot escape from the wells to recombine non-radiatively at surface states in the Si capping layer.

Furthermore, from time-resolved measurements a fast initial decay related to exciton and non-radiative and Auger recombination was found for the $\Delta_{z}$-valley related PL already for low excitation powers. This is in sharp contrast to the $\Delta_{y}$-related emission where much longer lifetimes have been observed. This behavior can be explained by a higher capture rate into the $\Delta_{y}$-valley compared to the $\Delta_{x}$-valleys as confirmed by a detailed fitting procedure leading to a quantitative determination of, exciton pair and Auger recombination rates. The presented results not only highlight a possible additional emission broadening process for SiGe/Si QDs but also have severe implications regarding the design of single photon sources based on SiGe QDs. Evidently, for such devices, suppressing the filling of different valleys by carefully adjusting the growth conditions (i.e., energetically lifting the $\Delta_{y}$-valley and shifting the HH wave-function away from the base of the SiGe island) or spatially controlling the e-h pair generation is essential.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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