Photoluminescence investigation of strictly ordered Ge dots grown on pit-patterned Si substrates

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Abstract
We investigate the optical properties of ordered Ge quantum dots (QDs) by means of microphotoluminescence spectroscopy (PL). These were grown on pit-patterned Si(001) substrates with a wide range of pit-periods and thus inter QD-distances (425–3400 nm). By exploiting almost arbitrary inter-QD distances achievable in this way we are able to choose the number of QDs that contribute to the PL emission in a range between 70 and less than three QDs. This well-defined system allows us to clarify, by PL-investigation, several points which are important for the understanding of the formation and optical properties of ordered QDs. We directly trace and quantify the amount of Ge transferred from the surrounding wetting layer (WL) to the QDs in the pits. Moreover, by exploiting different pit-shapes, we reveal the role of strain-induced activation energy barriers that have to be overcome for charge carriers generated outside the dots. These need to diffuse between the energy minimum of the WL in and between the pits, and the one in the QDs. In addition, we demonstrate that the WL in the pits is already severely intermixed with Si before upright QDs nucleate, which further enhances intermixing of ordered QDs as compared to QDs grown on planar substrates. Furthermore, we quantitatively determine the amount of Ge transferred by surface diffusion through the border region between planar and patterned substrate. This is important for the growth of ordered islands on patterned fields of finite size. We highlight that the Ge WL-facets in the pits act as PL emission centres, similar to upright QDs.

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(Some figures may appear in colour only in the online journal)

1. Introduction

SiGe quantum dots (QDs) formed during the heteroepitaxial growth of Ge on Si have been the subject of intense research [1–5], and self-organized nanostructure formation is probably best understood in this material system, which is also considered to be a prototypical system for heteroepitaxial strained...
layer growth. Many of its aspects can be transferred to other material systems such as e.g. InAs on GaAs(001) [5–7] or epitaxial group II–VI systems [5]. While the QD-growth mechanisms are fairly well understood, optical properties of SiGe nanostructures are more difficult to access. This is mainly caused by the poor light-emission properties of single SiGe QDs, owing to the indirect band-gap of the material. For ordered QDs, the density of the QDs is predefined by the substrate pattern. In contrast, on planar substrates, due to random QD-nucleation sites, the number of QDs contributing to the photoluminescence (PL) might vary for different positions of the micro-PL detection spot. However, information about the number of QDs contribution to the PL intensity is required to be able to carefully interpret the data as well as to suppress or reduce the inhomogeneous QD linewidth broadening of the PL-emission [8–14]. A promising way to exert precise control over the QDs density and their homogeneity, while additionally obtaining addressability, is the growth of QDs on pre-patterned substrates. Over the last years, numerous studies [6, 13–37] have been performed to improve position control of epitaxial QDs via substrate patterning. Very recently, we have shown that precise control of the inter-QD-spacing of strictly ordered QDs can be obtained on one-and-the-same sample for pit-periods ranging from ~400 nm to about 3400 nm [6]. Such a well-defined system with large inter-dot distances allows comparing the PL-emission of 100, 50, 25, 12, 6, 3 and one or two QDs with respect to each other and gives insight into the dynamics of QD-formation that is influenced by ad-atom redistribution from the wetting layer (WL) to the QDs in the pits. Our investigations address several interesting QDs-related physical and chemical phenomena which have evolved over the last years:

- We determine the role of QD growth due to WL thinning between the pits by varying the inter-QD-distances from 400 nm to 3400 nm and quantitatively investigating the respective confinement energy shifts of the WL-PL.
- By changing intentionally the original pit-shapes and -sizes and tracing the PL originating from the pits, we highlight the role of the activation energy barriers that have to be overcome for the positive charge carriers in the WL outside of the QDs in order to recombine within the pit-WL or within the QD. This refilling process is particularly important for low excitation intensities and large inter-QD distances, i.e. for potential single QD spectroscopy studies.
- Additionally, we show that micro-PL spectroscopy is a suitable tool to address intermixing effects in the WL, the WL in the pits and the QDs. We reveal that intermixing effects take place in the pits during Ge deposition already before upright QDs nucleate. This provides evidence that the initial intermixing in the pits causes the enhanced intermixing of the subsequently formed ordered QDs in contrast to randomly nucleated ones [13, 29, 30].
- It was shown in [31, 38] that Ge diffuses from the planar surroundings into the patterned field where pits and QDs attract material which leads to a WL thinning in the border regions outside the patterned fields. Additionally to the results in [31], here we can quantitatively determine, by PL-emission studies with high spatial resolution, the actual amounts of Ge diffusing to the patterned field and contributing to nanostructure growth.
- We show that facets decorating the pre-patterned pits act as PL-emission centres, similar to upright QDs.

This paper is organized as follows: In section 2 we describe the molecular beam epitaxy (MBE) growth procedure of highly ordered QDs on pit-patterned substrates with large pit-period variation from 425 nm to 3400 nm and the experimental conditions of the micro-PL measurements. In section 3.1 we describe the influence of the inter-QD spacing on the QD- and WL-related PL-emission, in section 3.2 we highlight the influence and importance of the initial pit-size and -shape on the QD, pit-WL and WL-related PL. In section 3.3 we proof that significant SiGe intermixing takes place in the pits before QDs actually nucleate there. Finally, in section 3.4 we present the PL-emission behaviour of the WL and the QDs in the border-region between pit-patterned and planar substrate with high spatial resolution before we conclude in section 4.

2. Substrate patterning, QD growth procedure and PL experiments

We patterned a high-resistivity (>1000 Ω cm) Si(001) substrate by means of electron beam lithography. Hereafter, we used reactive ion etching in order to transfer the pit-pattern into the substrate which results in approximately 47 nm deep cylindrical pits (see also [6]).

On one sample we wrote several fields with different inter-pit-periods (d_{pit}) ranging from 425 nm to 3400 nm. On a second sample we varied the pit-opening-diameter from 165 nm to 340 nm by varying the dose of the e-beam while leaving the respective d_{pit} constant. In all cases the size of the patterned fields was chosen to be 200×200 μm².

The samples were cleaned ex situ, and received a dip into diluted (1%) hydrofluoric acid to remove the natural oxide immediately before their introduction into a load-lock chamber. Growth was carried out in a Riber Siva 45 solid source MBE facility. After in situ degassing at 700 °C for 40 min, we grew a Si buffer layer by depositing 45 nm of Si at a growth rate of 0.6 Å s⁻¹ and at a growth temperature that was ramped up from 450 °C to 550 °C. The buffer layer step was finished by a ramp-up step to the respective growth temperature of Ge (T_{Ge}) during which both the Ge and the Si shutter were closed. Then, nominally three monolayers (MLs) of Ge were deposited at T_{Ge} = 700 °C and at a growth rate of 0.03 Å s⁻¹. In the last step we grew a 30 nm thick Si capping-layer at a growth temperature of 350 °C. As we will discuss in section 3.3, it is important to use such a low growth temperature for the capping-layer to preserve the physical and chemical properties of the WL [39] and the QDs [39, 40].

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After growth, the surface of the samples was characterized \textit{ex situ} using a Digital Instruments Dimension 3100 atomic force microscope (AFM) with sharpened Si tips having half-opening angles of 15° and nominal tip-radii of about 2 nm. In the following, the AFM images are presented either in the derivative mode or in the surface-angle image (SAI) mode, where the local surface slope is plotted with respect to the (001) substrate surface. For a more detailed description of the AFM representation modes, see e.g. [41].

Micro-PL measurements were carried out at sample temperatures set to 10 K. A frequency-doubled Nd:YVO$_4$ laser with an emission wavelength of 532 nm was used as an excitation source. The excitation power and beam diameter are 50 $\mu$W and less than 2 $\mu$m, respectively. The PL spectra were recorded using a liquid-nitrogen-cooled InGaAs line detector.

3. Results and discussion

3.1. Influence of the inter-QD distance on the QD and WL related PL-emission

Owing to the aforementioned, carefully adjusted growth conditions for the Si capping-layer, it is possible to obtain information about the surface morphology of the QDs despite the fact that the QDs are buried under Si. For instance, it is possible to detect whether there are imperfections in the two-dimensional alignment of the QDs. Imperfections in this sense are e.g. QDs not nucleating in the centre of the pit, missing QDs, double or multiple QDs per pit, but also secondary QDs nucleating between the pits. Figure 1 shows AFM images of the ordered QDs in the pit-patterned fields with different $d_{\text{pit}}$ ranging from 425 nm (figure 1(a)) to 3400 nm (figures 1(g) and (h)), presented in the derivative mode. The original pit-diameters and -depths were 197 nm and 47 nm, respectively. We stress that all fields shown in figure 1 were e-beam written on a single sample and therefore grown in one MBE growth run. Thus, it is remarkable that we observe independently of $d_{\text{pit}}$ that every pit hosts exactly one QD. Since the recipes for the substrate patterning as well as QD growth were exactly the same as for the QDs shown in the AFM images in [6], we know that also the QDs presented in this work are pyramids. Further, as shown in [6], the WL inhibits shape-transformation from pyramids to domes as a consequence of subtle energy-balance effects between WL surface-energies and QD-facet-formation energies. We deposited 3 ML of Ge at a growth temperature of 700 °C, i.e. less than the critical thickness of about 4.2 ML for QD-nucleation on planar substrates [42]. On the one hand, as the surface energy of a thin Ge WL ($\sim$ 5 ML) is increasing with decreasing WL-thickness [43]. On the other hand, a shape transition from pyramids to domes would involve QD-shapes with unfinished facets and, thus, with higher surface energy. Since pyramids require additional Ge for a shape-transition to domes, this shape-transformation cannot compete against WL thinning. Similar to the uncapped QDs presented in [6], it is evident from the AFM images presented in figure 1 that for the lowest $d_{\text{pit}}$ of 425 nm the pyramids have a slightly broader size distribution. From [6] it is also known that for the growth conditions used in this work the QD volumes slightly increase with increasing $d_{\text{pit}}$ for $d_{\text{pit}} < 2 \mu$m and saturate for $d_{\text{pit}} > 2 \mu$m at a value of about $5.5 \times 10^4$ nm$^3$.

Figure 2 presents micro-PL spectra obtained from the fields with different $d_{\text{pit}}$ that were presented in figure 1. The PL-bands that appear between 0.85 eV and 0.95 eV were previously assigned to the radiative recombination of
from the WL and pit-WL for the arrows in the topmost spectrum mark the two no-phonon transitions of the PL-emission and are guides for the eye. The two black dotted-line for the WL and QDs, respectively indicate the energy to WL thinning between the pits due to enhanced Ge mass-transfer to phonon (NP) line to higher energies with decreasing trend of the WL no-phonon (NP) peak to the Si capping-layer [47]. The known reference points are the energetic position of the WL-NP related peaks from any patterned positions of the NP-WL emission lines for the WL outside the pyramids and the WL in the pits (pit-PL) can be addressed later in section 3.2, when discussing the influence of the initial pit-opening size on the WL emission of the QDs and the WL. By comparing the emission energies originating from the WL-NP peak with previous data in [47], we are able to obtain a quantitative estimation of the actual thickness of the WL on the patterned fields as a function of $d_{\text{pit}}$.

Figure 2 allows addressing several points. There is a clear trend of the WL-related emission to shift to higher energies with decreasing $d_{\text{pit}}$. In [6], we have estimated the $d_{\text{pit}}$-dependent residual WL thickness between the pits from the pyramid volumes, the amount of Ge stored in the pit-WL and the degree of intermixing in the pyramids and the WL between the pits. For smaller $d_{\text{pit}}$ a comparably higher fraction of the totally deposited Ge per unit cell area ($d_{\text{pit}}^R$) is needed to form the QDs than for longer periods ($\sim 19\%$ of the totally deposited Ge is stored in the QDs for $d_{\text{pit}} = 425 \text{ nm}$ versus $0.4\%$ for $d_{\text{pit}} = 3400 \text{ nm}$). Accordingly, the calculated WL thickness increases from about 2.5 ML to 3 ML with increasing $d_{\text{pit}}$ [6]. This general trend can certainly be confirmed by the PL data in figure 2. The red-dashed line indicates the energetic position of the WL NP related peaks [45, 46] that, due to increasing quantum confinement with decreasing well width, shifts by 19 meV from 1030 meV for $d_{\text{pit}} = 3400 \text{ nm}$ to 1049 meV for $d_{\text{pit}} = 425 \text{ nm}$. Note that for $d_{\text{pit}} = 425 \text{ nm}$ two NP signals originating from the WL between the pits and the WL in the pits (pit-PL) can be identified, indicated in figure 2 by the two black arrows. We will address this point later in section 3.2, when discussing the shift of the PL emission energy to a WL thickness is possible despite the different capping layer growth temperature used in this work.

Figure 3 presents the shift of the PL emission energy of the WL-NP-peak with increasing WL thickness. Independently of the capping-layer growth temperature ($T_{\text{cap}}$), the WLs were always grown at 700 °C. However, different $T_{\text{caps}}$ of 300 °C, 500 °C and 700 °C (black, red and blue colour, respectively) were used in [39, 47] compared to this work ($T_{\text{cap}} = 350 \text{ °C}$). In order to correlate the results of this work to previous studies [39, 47] we proceed as follows: From figure 3 we know that the slope of the WL-NP peak position with increasing WL thickness is almost independent of $T_{\text{cap}}$. The WL-emission is only shifted to higher energies for higher $T_{\text{cap}}$ due to increased surface segregation of Ge from the WL to the Si capping-layer [47]. The known reference points are the WL-NP emission energy from areas far away (>2 mm) from any patterned field (i.e. not influenced by the patterned field, see figure 5) and the fact that we have deposited 3 ML of Ge. Thus, we create a line, parallel to the ones of $T_{\text{cap}} = 300 \text{ °C}$ and $T_{\text{cap}} = 500 \text{ °C}$ and in a way that the line...
includes the point (3 ML/1028.8 meV), i.e. the amount of deposited Ge and the energy of the NP-line of the WL on a non-patterned part of the sample. The light green points mark the energetic positions of the NP-WL emission lines originating from the WL outside the patterned field and between the pits for different pit-periods, as extracted from figure 2. The grey-shaded area and the black full arrows mark the uncertainty in the actual amount of deposited Ge that arises due to growth-rate fluctuations in the MBE system (<±4%). In such a way, an unambiguous assignment of the PL peak energy to a WL thickness is possible despite a different capping-layer growth temperature used in this work. Here, we find that the WL-thickness increases from 2.66 ML to 2.95 ML for \( d_{\text{pit}} \) ranging from 425 nm to 3400 nm which is in very good agreement with the estimation of the WL thickness between the pits presented in [6].

One additional observation can be made by looking at figure 3. It is remarkable that already for a 50 °C increase of \( T_{\text{cap}} \) from 300 °C to 350 °C the PL emission of the thin WL shifts by about 15 meV. Because of the capping-layer induced surface segregation of Ge affecting only the topmost MLs of the QD, it was shown for SiGe QDs that even a \( T_{\text{cap}} \) of 500 °C does not change the morphological properties and the energetic position of the PL-emission of the QDs [39]. On the other hand, seemingly minor segregation effects occurring in the topmost layers significantly change the WL confining potentials, and hence the PL emission properties. Thus, small Ge segregation effects during capping with Si can be traced in the WL much better than in the QDs that are usually tens or even hundreds of MLs thick [48].

Concerning the QD-related signal in figure 2, we observe a PL signal consisting of two peaks for all pit-periods: The peak at higher energies is ascribed to a NP transition, while a PL signal consisting of two peaks for all pit-periods: The even hundreds of MLs thick [48].

3.2. Influence of the initial pit-shape on the QD and WL related PL-emission

To obtain further insight into the aforementioned bimodal WL distribution which is observed on the field with \( d_{\text{pit}} = 425 \) nm (see figure 2, spectrum at the top) we investigate the influence of the initial pit size on the WL-, pit-WL and QD-PL characteristics. The left panels in figure 4 present height-mode AFM images of the different fields before growth where the average original pit-opening size was varied as follows: field (i) 340.6 ± 3.5 nm, field (ii) 283.7 ± 3.2 nm, field (iii) 219.9 ± 2.5 nm and field (iv) 164.8 ± 3.1 nm. The middle and right panels in figure 4 represent derivative-mode and SAI mode AFM images of the same fields after the deposition of the Si buffer layer, the Ge layer and the thin capping-layer (see section 2). As reported in [6, 19], it depends strongly on the interplay between the pit-shape after buffer layer growth and the Ge deposition parameters whether or not it is energetically favourable that upright QDs nucleate in the pits. For large initial pit-dimensions, i.e. field (i) and (ii), the amount of deposited material is only sufficient to decorate the facets of the pits, while for the smaller initial pit sizes (i.e. fields (iii) and (iv)) the provided material is sufficient to form small QDs as becomes clearly visible in the middle panels of figures 4(c) and (d). From uncapped samples grown on identical patterns and under the same growth conditions ([6]) we know that those QDs are pyramids.

Figure 5 depicts micro-PL spectra taken from field (i) to field (iv) of the Si-capped samples depicted in figure 4, for which the initial pit-opening size was varied. The topmost spectrum (black colour) was recorded far away (>2 mm) from the patterned fields and shows a typical WL-related PL signal with NP-peak, transversal acoustical phonon peak (TA) and the Si–Si, Si–Ge and Ge–Ge related transversal optical phonon peaks [45], as indicated in figure 5.

In the spectra obtained from the patterned fields the prominent NP and TG\(^{\text{Si–Si}}\) related transitions are indicated by solid and dashed arrows, respectively. The QD-PL-peak obtained from field (iii) is shifted by 14 meV to higher energies with respect to the one of the field (iv). Again, a comparison with the AFM data, especially the AFM data presented in SAI mode can explain this blue-shift. From the SAI mode images in figures 4(c) and (d) one not only finds that the pit-sidewall angle decreases from about 8° to 6° for field (iii) to about 5° for field (iv), but also that the inclination of the facets of the QDs in the pits increases. The QDs in field (iii) have lower height and thus, the PL-transition-energy from those QDs is increased due to increased quantum confinement. The reason for the smaller QD size is simply that due to the larger initial pit diameter in field (iii) as compared to field (iv) (see figures 4(c) and (d), left hand side), more material is needed to decorate the pit-WL and thus less material is available to form the QDs. For even larger initial pit diameters (see figures 4(a) and (b)), no upright QDs are found in the pits, despite the fact that the pit-sidewall inclination angles are still in the optimal range between 5° and 18° for which QD growth occurs in the middle of the pits [6, 19].

In figure 5 the blue and green arrows indicate WL between the pits- and pit-WL-related PL-transitions. In figure 6 we plot the full-width at half-maximum (FWHM) of the NP transition as function of \( d_{\text{pit}} \) (left panel) and the original pit-opening diameter (right panel). The FWHM was determined from fits of the NP-PL peaks using Gaussian functions. In combination with the AFM images presented in figure 4 the distinct difference in the FWHM of the NP-peaks allows us to identify contributions originating from the WL in between the pits (FWHM \( \approx 10 \) nm) and the pit-WL (FWHM \( \approx 20 \) nm). The significantly larger FWHM of the NP pit-WL-PL emission is probably caused by more inhomogeneous SiGe alloying in the pit-WL, as compared to the more homogeneous Ge composition WL between the pits. In figure 5, field (iv) we find a bimodal nature of the WL-related
PL-emission. This implies that there must exist at least three spatially separated regions from which the WL-, pit-WL- and QD-PL originate that are also energetically separated by an activation energy barrier. The three NP peaks and the concomitant TO-phonon assisted peaks are indicated in figure 5 by the solid and dashed arrows, respectively. We stress again that the AFM micrographs in figure 4 show that small QDs are present in the pits after Ge deposition on these fields with small original pit-diameters. In figure 5, the emission bands originating from the QDs are indicated by the red arrows.

It should be noted, that on the planar part of the sample there are no QDs, since the deposited amount of Ge did not exceed the critical amount for QD nucleation at this growth temperature (700 °C) which is about ∼4.2 ML. Typically, for deposition of Ge above the critical thickness, one observes PL originating from randomly nucleated QDs and the WL at different energies. For randomly nucleated QDs on planar substrates, the charge carriers have to overcome an energy-barrier formed by a thinner WL surrounding the QDs in order to drift to the global energy minima in the QDs. This WL

Figure 4. AFM images: influence of the pit-dimensions on the surface morphology after the overgrowth with a 45 nm thick Si buffer layer, 3 ML of Ge and a 30 nm Si capping-layer. The pit diameters before growth are (a) 340 nm, (b) 284 nm, (c) 220 nm and (d) 165 nm and the initial pit depth was 47 nm in all cases. \( d_{\text{pit}} \) is 425 nm for all fields. (a)–(d) left column: AFM height-images of the pits before MBE growth. Middle column: AFM images in the derivative mode after the growth sequence. Right column: same recorded files as in the middle row but presented in SAI mode. The colour coding in the SAI images was chosen in such a way that for inclinations <10° the colour changes from white to violet every 2°, see colour bar below the panels. Additionally, the stable Ge [105]-facet (11.3°) is indicated by a blue colour.
thinning and even formation of trenches in the substrate [48–50] is caused by the compressive in-plane strain, induced in the substrate below the circumference of the QDs (domes and pyramids) and is a result of the elastic relaxation of the QDs [49]. The situation seems to be similar for the QDs grown on pit-patterned substrates. By selective etching of the thin WL, Zhang et al [51] found evidence for such regions of thinner WL separating the Ge-rich WL [47] on the planar (001)-oriented parts between the pits and the pit-WL. In the light of these findings, we attribute the PL emission bands seen in figure 5 for the field (iv) to carrier recombination paths in the QDs, the pit-WL and the WL between the pits.

3.3. Intermixing effects in the pits prior to QD growth

Next, we address the role of intermixing in the pit-WL. Schülli et al [29] and Pezzoli et al [30] have shown by means of high-resolution x-ray diffraction and selective etching experiments that intermixing of Ge with the underlying Si is enhanced for QDs grown on pit-patterned substrates, as compared to the growth on planar substrates. From the PL results presented in figure 5 additional information can be deduced. We show that on pit-patterned substrates the WL in the pits is already intermixed with Si prior to QD nucleation. In field (i) ($d_{\text{pit}} = 425$ nm and an original pit-opening size of 340 nm), no QDs have evolved in the pits. The PL emission comes therefore from the pit-WL (see figure 4(a)) and is shifted by 11.3 meV to higher energies with respect to the one of the flat WL on a planar substrate (black spectrum at the top of figure 5). We will show that this blue-shift can be explained by SiGe intermixing effects in the pit-WL. At first we need to rule out that the pit-induced increase of the substrate surface causes the pronounced blue-shift in the PL spectra in figure 5. After buffer layer and Ge growth the surface-increase induced by the pit-patterning in field (i), accounts to only about 0.8% as compared to a planar (001) substrate. Assuming the unrealistic case of conformal Ge overgrowth [6, 25, 32] that would cause the highest blue-shift of the WL-PL-emission, the WL thickness would be then 2.976 ML instead of 3 ML on a planar substrate. From the data in figure 3 we see that such a WL thickness reduction would only amount to a PL-blue-shift of 1.2 meV. The observed blue-shift is, however, 11.3 meV. Thus, we can rule out that solely WL thinning caused by an increased sample surface on the pit-patterned field leads to the aforementioned blue-shift. In fact, it has been shown that the WL does not grow in a conformal way, see e.g. in [6, 25, 32] which leads to regions of thinner and thicker Ge layers. The latter are the energetic minima due to lower confinement energy. Therefore, non-conformal WL growth in the pits would lead to a lower PL transition energy from the pit-WL than for the WL on planar (001) substrates. In the case of field (i) this effect is

Figure 5. Micro-PL spectra taken from the samples depicted in figure 3. The spectra are vertically shifted for reasons of clarity. Top: spectrum of the WL recorded far away from the patterned fields. The optical transitions from NP-transition, and TA and TO-phonon assisted transitions are indicated by arrows. In the spectra related to the patterned fields only the NP and TO$^{\text{Si-Si}}$ related transitions are indicated by solid and dashed arrows, respectively. Red arrows indicate QD-related transitions and green and blue arrows pit-WL- and WL between pit-related optical transitions.

Figure 6. Full-width at half-maximum of the no-phonon peaks of the PL-signal originating from the WL-between the pits (blue), the pit-WL (green) and the WL on planar substrate (black) as function of $d_{\text{pit}}$ and the initial pit-opening size. The NP-PL peaks were fitted using Gaussian functions.

6 Other mechanisms explaining the observed blue-shift might arise from carriers being confined in specific regions of the WL, for instance at the edges or the bottom of the pits due to local energy minima given for instance by local strain or alloy variations. However, such specific regions were not found using selective wet chemical etching of pyramids grown on pit-patterned substrates [21].
overruled by Si–Ge intermixing effects which cause a shift of the PL-emission of field (i) to higher energies. This is a direct proof that on the surface of pit-patterned substrates Si is available even before QD nucleation (as theoretically predicted in [32]) leading to the homogeneous composition profiles of ordered QDs observed in [29, 30]. This is in strong contrast to QDs grown on planar substrates, where the WL remains Ge-rich [47] before trenches in the substrate develop at the periphery of the QDs [48–50].

3.4. PL-emission properties of the WL and QDs at the border between patterned and planar substrate

Finally, to understand the impact of the surrounding of the patterned field, we investigated the PL spectra obtained from the border-region of the field. Previous works have shown that the pits [31, 38, 52] and QDs in the pits that exhibit unfinished facets play the role of material sinks [31], which leads to a concentration gradient that causes diffusion of Ge from the near surroundings of the patterned field into the pits of the substrate [31, 38]. Such material flow influences the morphology of the QDs in the pits and in the surrounding planar part of the sample and can reach length scales of several tens of micrometres [31]. To address quantitatively the Ge amount transferred at the border between planar and patterned area, we focus on the PL from QDs, WL and pit-WL.

Figures 7(a)–(c) present AFM images from (a) the planar part of the sample, 40 μm away from the border to the pit-patterned field, (b) the border region between the planar part and the patterned field and (c) the middle of the patterned field with a pit diameter of 425 nm. On the planar part of the sample no QDs exist. On the border between the planar part and the patterned part we see QDs in the pits. This is because a concentration gradient of mobile Ge on the surface drives diffusion of Ge into the patterned field where, once enough material is accumulated, QDs start to form in the pits [31]. In the middle of the patterned field, no upright QDs, but only a facetted pit-WL exists.

In Figure 7(d) five selected PL-spectra are presented taken at the distance x between the planar and the patterned part of the substrate of x = –60 μm, x = –7 μm, x = 0 μm, x = 7 μm and x = 60 μm. Negative and positive directions refer to the planar part and the patterned part of the substrate, respectively, while x = 0 μm describes the border between the two parts. In figure 7(e) a 2D-representation of the change of the WL- and QD-related PL is shown as a function of the distance x. The spectra were recorded starting from the planar part, approximately 70 μm outside the field and ending directly in the centre of the patterned field at x = 100 μm. The planar WL-PL

Figure 7. (a)–(c) AFM images in derivative mode. (a) AFM image taken on the un-patterned part x = –40 μm away from the border of the patterned field (field (ii), dpit = 425 nm), (b) from the border between the planar and the patterned field at x = 0 μm (c) from the middle of the field, i.e. x = 100 μm. (d) Spatially resolved PL-spectra for x = –60 μm, –7 μm, 0 μm, 7 μm and x = 60 μm. (e) Contour plot of the spatially resolved PL-spectra as a function of the distance between the planar and the patterned part of the substrate. (f) Integrated intensity of the WL (red squares) and the QDs (blue circles) versus x at the border of the patterned field. The integrated WL (QD) intensity drops (increases) from 80% (20%) to 20% (80%) of its maximum intensity within 4 μm (4.8 μm).
exhibits a pronounced blue-shift towards the border of the patterned field which can be explained by the increasing quantum confinement energy of the thinner WL near the border. This reduced WL thickness is caused by the aforementioned Ge flow from the planar part of the substrate to the patterned field, as evidenced in detail by AFM measurements in [31]. To obtain further insight we determine quantitatively the amount of Ge that is actually transferred during this depletion process based on the PL emission energy shown in figure 3 in section 3.1. The WL emission energy at $x = -70 \mu m$ is at 1028.8 meV, which corresponds to a WL thickness of 3 ML, while the WL-emission energy at the border (at $x = 0 \mu m$) is 1056.6 meV, corresponding to a WL thickness of 2.57 ML. Furthermore, in figure 7(e) the PL-energy shift appears even at a position of $50 \mu m$ away from the border, meaning that WL-thinning occurs even there, owing to the long surface diffusion lengths in the system [31, 38].

We found from the AFM images that small upright QDs exist even at a distance of $x = 15 \mu m$. In the PL shown in figure 7(e), two slopes in the QD and pit-WL-related blue-shift of the PL are visible. Between 0 and $15 \mu m$ into the patterned field, where the PL blue shift is stronger, we find in the AFM scans upright QDs in the pits with decreasing height and finally, for distances larger than $15 \mu m$ away from the border in the patterned field no convex structures are found in the pits. The shift of the PL signal to higher energies for a distance between $x = 15 \mu m$ and $x = 100 \mu m$ can be attributed to a monotonous decrease of the amount of Ge in the pit-WL, i.e. the pit-WL is thinner and thus, the PL is shifted to higher energies. This interpretation is consistent with the WL thinning that is owed to surface diffusion of Ge between the planar and patterned areas, as described above.

By using micro-PL measurements with high spatial resolution and a sharp change in the sample environment we evaluate the PL detection spot size using the AFM images and a ‘modified knife edge method’. While the diameter of the excitation spot is limited by the focusing optics to about 1–2 µm, the detection spot size actually determines how many QDs contribute to the PL signal. Figure 7(f) shows how the integrated intensity of the WL-PL and QD-PL changes at the interface between the planar and the patterned area of the sample. The spot size is determined from the distance, by which the WL-PL intensity decreases from 80% to 20% and the QD-PL intensity increases from 20% to 80% of its maximum value. In both cases, the detection spot diameter was determined to be 4–4.8 µm. Such a small detection spot allows us to quantify the number of QDs that effectively contribute to the QD-related PL signal presented in figure 2. For the field with $d_{pit} = 425 nm$ about 70 QDs are contributing, while for the $d_{pit}$ of 600 nm, 850 nm, 1200 nm 1700 nm and 2400 nm, 35, about 18, 9, 5 and about 3 QDs contribute, respectively. For the largest pit-period under investigation, 3400 nm, it depends on the exact location of the detection spot whether the PL is collected from one or two QDs. This is schematically depicted in figure 1(h). Depending on the pick-up position, either one or two QDs are fully contributing to the collected PL signal. Such a situation with low QD densities and a small PL detection spot is promising for future examinations of the optical properties of single and few QDs with type-II band alignment. In-depth investigations of the optical properties of single SiGe QDs will be presented in a forthcoming publication [53].

4. Conclusion

We investigated the optical properties of strictly ordered Ge QDs, grown on pit-patterned Si(001) substrates with a wide range of pit-periods (425–3400 nm) using micro-PL spectroscopy. Using pits with different shapes and sizes allowed us to determine the influence of strain-induced activation energy barriers on the ordered-QL-PL. In addition, we demonstrated that the WL in the pits is already severely intermixed with Si before QDs nucleate leading later to the enhanced intermixing of ordered QDs as compared to randomly nucleated ones. We quantitatively determined the amount of Ge transferred by surface diffusion through the border region between the planar and the patterned part of the substrate, which is important for the growth of ordered islands on patterned fields with finite sizes. We showed that the Ge WL forming crystal facets in the pits acts as an effective PL emission centre, similar to ‘upright’ QDs. As an outlook, we have shown that tuning the inter-QD-distance is a key to the optical addressability of precise numbers of QDs, between one and one-hundred in this work. Ordered QDs on pit-patterned substrates will be interesting for future examination of the optical properties of single and few QDs with type-II band edge alignments.

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Authors’ contributions

MG and MB contributed equally to the work in designing the experiment and the samples, carrying out the experiments, the experimental analysis and writing the manuscript. MG, MB and TT carried out PL experiments. GL fabricated substrate templates and contributed to their design. TT, GL, TF, OGS and FS contributed to the manuscript design and all authors discussed the manuscript.

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