Atomic structure and composition distribution in wetting layers and islands of germanium grown on silicon (001) substrates

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Abstract

We present a comprehensive structural investigation of the Ge wetting layer (WL) and island growth on Si(001) substrates by a combination of AFM, high resolution transmission electron microscopy and the energy-differential coherent Bragg rod analysis (COBRA) x-ray method. By considering the influence of the initial Si surface morphology on the deposited Ge, these techniques provide quantitative information on the Ge content and its distribution, in particular within the WL which plays a crucial role in the formation of epitaxial nanostructures. In the WL, the Ge content was found to be above 80% for our growth conditions. Furthermore, from the digital analysis of high-resolution transmission electron microscope images, quantitative information on the strain relaxation is obtained, which complements the COBRA analysis of the Ge distribution and content in these nanostructures.

Keywords: Si–Ge quantum dots, nanostructures, HRTEM, COBRA, AFM, Stranski–Krastanow

1. Introduction

The deposition of Ge on Si substrates has been studied extensively as a prototypical system for the formation of thin, strained heteroepitaxial layers. In particular the process of island growth, essentially following the Stranski–Krastanow model, has been investigated quite thoroughly (Eaglesham and Cerullo 1990, Mo et al 1990, Medeiros-Ribeiro et al 1998, Brunner 2002, Teichert 2002, Baribeau et al 2006, Tsybetsk and Lockwood 2009, Aqua et al 2013, Zhang et al 2015). According to this model for growth on a lattice mismatched substrate, in our case silicon, first a biaxially strained Ge-rich wetting layer (WL) grows, in which the accumulated strain can only be partially relieved by surface reconstruction.

However, beyond a certain critical thickness, further strain relief sets in through island nucleation.

Until recently, the commonly accepted sequence of island shapes with increasing Ge deposition was one in which pre-pyramids first appear, followed by pyramids, domes, barns (Rastelli et al 2006) and finally cupolas (Brehm et al 2011b). In this sequence the aspect ratio of the different island shapes increases, thus promoting strain relaxation.
However, in recent years it was found that supersaturation effects in the WL of the Ge on Si system (Schittenhelm et al 1995, Sunnamura et al 1995, Brehm et al 2009b), as well as that of InAs on GaAs (Placidi et al 2005, Tsukamoto et al 2006) prior to elastic relaxation, are decisive for the formation and shape of growing islands. The supersaturation manifests itself in one full monolayer of deposited adatoms moving on the WL surface without being incorporated (Tsukamoto et al 2006) which has significant consequences for epitaxial nanostructure formation (Zhang et al 2015). By exploiting this mobile adatom layer during growth, it is possible to obtain assemblies of highly uniform and unimodal dome islands (Brehm et al 2009b), defect-free, in-plane nanowires of several micrometer length (Zhang et al 2012) and ordered quantum dots and quantum dot-molecules of arbitrary density (Grydlik et al 2012, 2013).

The physical origin of the WL supersaturation is based on a complex interplay between the surface energies of the WL and the islands. The former highly depends on the actual thickness of the WL, since, for thin layers, the stronger substrate bonds below the WL still influence the surface energies (Beck et al 2004, Lu et al 2005). The latter depends on the crystal facets of the respective islands. Using model calculations assuming a Ge content in the WL of 100%, (Brehm et al 2009b) predicted supersaturation of the WL and an enhanced thermodynamic stability of larger domes over smaller pyramids grown on thin WLs, as experimentally observed. Because the surface energies as well as the surface kinetics are influenced by the presence of Si on the surface, it is of particular relevance to obtain precise information on the Ge content and its distribution within the WL. This is essential for understanding the mechanism by which surface nanostructures form and assessing the role of chemical intermixing.

Despite the deposition of pure Ge during growth, it is well known that moderate Si intermixing from the substrate occurs in the growing WL (Brehm et al 2008) and to a larger extent within the islands (Medeiros-Ribeiro et al 1998, Hadjiasvass and Kelires 2005, Schülli et al 2005, Leite et al 2007, Marzegalli et al 2007, Rastelli et al 2008, Baskaran and Smereka 2012). The amount of intermixing depends critically on the chosen growth conditions.

A number of different experimental techniques have been employed to investigate the chemical composition of both the WL and the islands, including transmission electron microscopy (Stenkamp and Jäger 1993, Liao et al 1997, Chaparro et al 1999, Kienzle et al 1999, Kret et al 2001, Rosenauer 2003), quantitative energy-dispersive x-ray spectroscopy (Norris et al 2014) or electron energy loss spectroscopy (EELS) (Walther et al 1997) in scanning transmission electron microscopy (STEM) (Norris et al 2014), x-ray diffraction (Schmidbauer 2004, Stangl et al 2004, Biasiol and Heun 2011, Hrauda et al 2011) and selective chemical etching combined with scanning probe microscopy (Rastelli et al 2008, Pezzoli et al 2009). In addition, optical techniques such as photoluminescence (Schittenhelm et al 1995, Sunnamura et al 1995, Schmidt et al 1999, Lo et al 2001, Kamenev et al 2004, Grydlik et al 2010, Brehm et al 2011a) and Raman spectroscopy (Wan et al 2001, Pezzoli et al 2008, Bonera et al 2009, Picco et al 2010, Mala et al 2014) have also provided useful insights.

Quite a number of techniques, such as surface x-ray diffraction (Zhou et al 2011), Rutherford backscattering (Nakajima et al 1999), x-ray photoelectron diffraction (Gunnella et al 1996), Auger electron diffraction (Gunnella et al 1996), photoluminescence (Brehm et al 2008, 2009a, 2011a), as well as EDX and EELS combined with STEM (Walther et al 1997, Norris et al 2014), were used to obtain information on Ge–Si intermixing in the WL. However, not all of these investigations resulted in similar values for the Ge content of the WL. *Ab initio* density functional theory calculations (Beck et al 2004, Lu et al 2005, Montalenti et al 2013) of the dependence of the chemical potential on the number of deposited monolayers of Ge on Si have shown that for the first two monolayers the chemical potential is even lower than for unstrained Ge and approaches the value of bulk Ge only at about five monolayers. This result has been invoked to explain a comparatively high Ge content of the WL found e.g. in photo-luminescence (PL) experiments (Brehm et al 2008) with a peak value as much as 86% (Brehm et al 2008).

As SiGe intermixing in the WL is of high importance for the subsequent nanostructure formation, it is the purpose of this manuscript to provide a thorough study on the evolution of the layer-by-layer resolved Ge content of the WL and subsequent islands. We employ a combination of complementary characterization techniques for this purpose, which allow us to critically cross check features determined by different methods. These include atomic force microscopy (AFM), digital analysis of lattice fringe images (DALI) (Rosenauer et al 1996, 1997, Kret et al 2001, Rosenauer 2003) obtained by high-resolution transmission electron microscopy (HRTEM), and the energy-differential coherent Bragg rod analysis (COBRA) x-ray method which utilizes a phase retrieval algorithm (Yacoby et al 2002, Kumah et al 2009). Whereas HRTEM information is obtained on a rather small sample volume, the COBRA method provides data on sufficiently large sample volumes to be representative for the entire sample. Furthermore, the energy differential COBRA method provides quantitative mono-layer by mono-layer chemical composition information. Thus the Ge concentration profile obtained by the COBRA method, i.e. the structural and chemical information can be compared with determinations based on PL measurements. Note also that the Ge content and profiles can only be determined from PL if additionally a Si surface capping layer is grown and which, however, rely on numerical simulations of the electronic structure of the WL (Brehm et al 2008).

Most importantly, in this work, we consider also the fact that Ge is not deposited directly on an atomically smooth Si (001) substrate, but on a stepped surface upon which a silicon epilayer, a so-called Si buffer layer, is deposited, to secure a high structural quality of the subsequent Ge growth. Under these conditions the silicon epilayer can exhibit a surface undulation caused by step-bunching (Mysliveček et al 2002), which has to be considered in the proper interpretation of
x-ray surface scattering data comprising information from a large sample surface and volume. This is of particular importance for the correct determination of the Ge profile in the few monolayer thin WL and was so far not taken into account in the literature.

The manuscript is organized as follows: in section 2, information on the sample growth and its characterization by AFM and HRTEM is presented. In section 3, we describe the TEM data and the DALI analysis, both of the WL and of the islands, followed by a presentation of the COBRA measurements and their analysis. The results are discussed in section 4 and summarized in section 5.

2. Experimental section

2.1. Molecular beam epitaxial growth

The samples investigated in this work were grown on high-resistivity (>1000 Ω cm) 4 inch Si(001) wafers in a Riber SIVA45 solid-source molecular beam epitaxy system. After ex situ sample cleaning we performed an in situ oxide desorption step at 950 °C for 15 min. Thereafter, a Si buffer layer was grown with a thickness of 45 nm while the substrate temperature was ramped up from 450 °C to 550 °C. The growth rate for the Si buffer was 0.6 Å s⁻¹. For the subsequent deposition of Ge, the growth temperature was ramped-up to 625 °C and stabilized, and then 10 Å of Ge were deposited at a growth rate of 0.15 Å s⁻¹. After the Ge deposition, the growth temperature was immediately ramped-down to 350 °C and at this temperature a capping layer of 2 nm of Si was deposited at a rate of 0.4 Å s⁻¹. Such a low capping layer growth temperature has no detrimental effect on the islands and especially the thin WL, i.e. no appreciable alloying occurs (Brehm et al 2008, 2011a).

2.2. Surface analysis by AFM

AFM experiments were performed ex situ using a Veeco Nanoscope 3100 instrument operating in tapping mode. We used sharpened tips with a 2 nm tip radius and a half tip opening angle of 15°. Figure 1(a) presents a topographic AFM image of the sample surface after the growth. By plotting the AFM data as a surface angle image (SAI) (Brehm et al 2011b) (see figure 1(c)) larger domes (Medeiros-Ribeiro et al 1998) and smaller pyramids (Mo et al 1990, Teichert 2002) can be easily identified (Rastelli et al 2006), consistent with these earlier reports. In SAI, the local surface slope is plotted with respect to the (001) surface. This image representation mode emphasizes the island facets, as different facets are highlighted by different colors (Brehm et al 2011b). The presence of this bimodal island shape distribution of domes and pyramids is again highlighted in figure 1(b) where the statistical distribution of island heights is plotted, indicating two well-defined peaks: pyramids (blue color), with average height of 4 nm, and domes (orange color) with average height of about 11 nm. The domes and pyramids have areal densities of ~5.7 × 10⁹ cm⁻² and 3.8 × 10⁹ cm⁻², respectively. However, due to the significantly larger volume of the domes with respect to the pyramids, the domes contribute about 88.2% of the total island volume whereas the pyramid-volume amounts to only about 11.8% of the total.

Figure 1(d) and the inset in figure 1(d) present 15 × 15 μm² and 2.5 × 2.5 μm² AFM micrographs for which the color scale is chosen to be sensitive to the first nanometer of the sample surface, while the islands themselves are out of scale and appear as white dots. The overall surface roughness, excluding the islands (presented in figure 1(d)), is relatively low (rms = 0.23 nm) but step-bunching effects originating from the original Si buffer layer growth are clearly present. These step-bunching-induced local height differences are up to 1.2 nm (see figure 1(d)). Step-bunching (Schelling et al 1999, Mysliveček et al 2002) is a kinetically driven
growth instability that leads to the formation of ripples on slightly vicinal Si(001) surfaces during Si homoepitaxy (i.e. for non-strained systems). This instability is observed when the interplay between diffusion anisotropy and step-edge detachment behaves like an effective (and temperature-dependent) inverse Ehrlich–Schwoebel barrier (Schwoebel and Shipsey 1966) at certain surface step-edges. In (Mysliveček et al. 2002) it was shown that this two-dimensional (2D) diffusion anisotropy, which is always present on a \((2 \times 1)\) reconstructed Si(001) surface, causes this unstable growth. It is important to mention that the Ge WL growth replicates the step-bunches that occur during the growth of the Si-buffer layer. The WL, which is only a few tenths of a nanometer thick, cannot planarize these height differences and hence the islands nucleate on areas that show local height differences at their base, up to about 1.2 nm. The consequences of this height modulation for the interpretation of the COBRA data will be discussed in section 4.

### 2.3. High-resolution transmission electron microscopy

The cross-sectional HRTEM investigations were performed using specimens thinned with standard preparation methods. The final thinning of the specimens was performed by dimpling and Ar-ion sputtering with acceleration voltages in the range of 1–2 kV. The samples were investigated using a Philips CM200 TEM at 200 kV and an FEI TITAN\(^3\) 80–300 at 300 kV, the latter equipped with an image aberration corrector (C\(_c\)-corrector). The HRTEM images of the islands and the WL were analyzed using the DALI software (Rosenauer 1996, 1997, 2003, Kret et al. 2001) to derive the local lattice displacements and to obtain average values of the local lattice-parameters within dome-shaped islands and the WL. The analysis is based on the comparison of a reference lattice with the measured one and proceeds via the following steps: first, if necessary, Fourier Wiener filter (Rosenauer 2003) procedures are performed to improve the signal-to-noise ratio of the image; next, intensity maximum positions are determined. These positions may not exactly coincide with the real lattice sites, because HRTEM contrast depends on the chosen defocus value and local sample thickness. However, the intensity maximum positions accurately represent distances between lattice sites if the TEM specimen thickness does not significantly change in the evaluated region of the HRTEM image. Our analyzed regions are small enough that a constant thickness and defocus value can be assumed. Keeping this in mind, we will in the following denote intensity maximum positions as lattice sites. In the next step, a grid is generated by connecting lattice sites along two selected directions. The grid in the undistorted Si-substrate is considered as a reference lattice, which is extrapolated into the WL and the islands. Finally, displacements between the actual lattice sites and the corresponding reference lattice sites are determined from which local lattice-plane distances can be calculated.

For correct interpretation of the DALI data from a strained heterostructure system it is necessary to take into account that the lattice sites are influenced by bending of the atomic columns along the electron path even if the cut through the island exhibits constant thickness. Especially in three-dimensional islands, in which strain relaxation takes place in all three space directions, the atomic columns are typically bent (Schülli et al. 2003) and thus not parallel to the electron beam. Furthermore, due to the small thickness of the TEM specimen, partial relaxation from the biaxial strain state in the electron-beam direction is unavoidable. This leads to an overestimation of the strain in the substrate, and a concomitant underestimation of the island’s strain. Consequently, DALI provides qualitative information about the relaxation in the dome-shaped islands, and the quantitative values are subject to errors which are not negligibly small. Correction of the relaxation would be possible by simulations, e.g. involving finite element calculations, which would allow disentangling quantitatively the influence of strain and of composition on the lattice parameter. In section 3.2 we will further explore how the effects of strain and composition can be de-convoluted, using the differential COBRA method.

### 3. Results

#### 3.1. HRTEM studies of the WL and islands

Figure 2(a) shows a \([110]\) zone-axis HRTEM image of an island recorded with the Cs-corrected TITAN\(^3\) 80–300. One can identify the prominent \([113]\) facets of this dome-shaped island. The specimen is sufficiently thin for DALI analysis, and the cross-sectional cut is through the middle of the dome-shaped island. No discontinuities of the lattice planes across the interface are visible. This image was noise filtered by the Fourier Wiener filter method (Rosenauer 2003) and additionally \([111]\)-Bragg-filtered to use only the information stemming from the \([111]\)-reflections. With a sufficiently large aperture, this can be done for a perfectly crystalline WL and island without introducing artifacts. Figures 2(b) and (c) display a perspective view on the substrate and island lattice planes to show the coherence at their interface and to highlight the lattice-plane bending in the island close to its apex. No lattice plane bending is visible in figure 2(b), whereas a clear deviation from flat lattice planes is visible near the island apex, see figure 2(c).

Figures 3(a) and (b) present DALI maps of the local displacement of the gridded lattice-sites relative to the reference lattice. For this analysis the reference lattice was defined over a sufficiently large area in the Si-substrate to define the reference lattice in the strain-free substrate region (marked by the dashed red rectangle). This assures that the bulk lattice parameter of silicon, \(a_{\text{ref}}\) (and the respective lattice plane distances \(d_{\text{ref}}\)), are established as a reference. Since the right-hand part of the island shown in figure 2(a) contains TEM-sample preparation artifacts, only the high-quality left-hand part was analyzed. In figure 3(a) the local vertical displacements with respect to the reference lattice are displayed for the \((002)\) lattice planes and in figure 3(b) for the \((\bar{2}20)\) lattice planes. The \([001]\) and \([1\bar{1}0]\)-displacement directions,
indicated in figures 3(a) and (b), are oriented perpendicular to the corresponding planes. The color-coded displacements are normalized with respect to the Si(002) (figure 3(a)) and Si(220) lattice-plane distances (figure 3(b)). A displacement of ‘1’ indicates that a position of the real lattice is displaced by one lattice-plane distance compared to the respective lattice-site in the Si-reference lattice. Figure 3(a) shows that the displacements in the [001] direction increase from zero within the substrate to almost 1.2 (002) lattice planes at the apex of the dome-shaped islands.

Figure 3(c) plots the displacements of the (002) planes in the center part of the island as a function of the (002) plane number in the growth direction. The displacement was averaged along each (002) plane within the red frame shown in figure 3(a). As expected, the displacements in the Si-substrate do not significantly deviate from zero. The region from 0 to 4 (002) lattice planes corresponds to the (WL). The increase of the displacement from the island/WL interface to the island’s top exhibits a nearly linear behavior which is in agreement with previously reported data obtained from the analysis of anomalous x-ray diffraction data from dome-shaped islands (Schulli et al 2003). We deduce an accumulated displacement of 1.2 for 40 (002) lattice planes, which corresponds to a (002) lattice spacing of 1.03 $d_{\text{ref}}$. This means the (002) lattice spacing at the apex of the island is ~3% larger than that of Si.

In figure 3(b) we mapped the displacement of the (220) planes, which are bent away from the island center. Along the surface of the {113}-facet the accumulated displacement amounts to values between 0.4 and 0.6 of the interplanar spacing, which results from accumulation of the enlarged SiGe (220) lattice plane distances starting from the center of the island and increasing approximately linearly towards the side facets. This allows to approximately determine the average lattice parameter parallel to the (220) planes as $1.012 \pm 0.004 \times d_{(220)\text{ref}}$. For a region in the lower part of the island between the side facet and the center, the DALI analysis thus yields an average tetragonal lattice unit cell with an approximate height of 1.03 $d_{(002)\text{ref}}$ and base square area of $(1.012 \times d_{(220)\text{ref}})^2$.

3.2. Energy-differential COBRA

The atomic structure and Ge distribution were investigated using the COBRA method (Yacoby et al 2002, Kumah et al 2009). Due to the large footprint of the x-rays on the sample, a much larger sample volume is investigated as compared to TEM. The x-ray diffraction intensities were measured along ten substrate-defined symmetry inequivalent
Bragg rods at beam-line ID33-D of the Advanced Photon Source, Argonne National Laboratory. The sample was mounted on a Kappa goniometer and the x-ray intensities were measured using a Pilatus area detector. Prior to these measurements, the goniometer was calibrated and its performance tested by measuring the tracking accuracy of an auto-collimator mounted on the detector arm and a mirror mounted on the sample stage. The tracking was found to be within 300 micro-radians. The data were analyzed using the COBRA phase-retrieval algorithm (Yacoby et al 2002). In general COBRA determines the real space electron density of epitaxial thin films periodic in 2D with a period equal to that of the crystalline substrate. If however, the structure is not periodic in 2D or its period differs from that of the substrate we need to consider the folded structure (Yacoby et al 2000). The folded structure is obtained by translating each atom in the system to one substrate-defined 2D unit cell using substrate-defined unit cell vectors. If the atoms in the film are registered relative to the substrate atoms the folded electron density is not constant and can be determined by COBRA. Epitaxial quantum dots are not periodic in 2D but if the atoms are registered with respect to the substrate atoms, the electron density of the folded structure is not a constant and can be determined by COBRA providing detailed structural information about the quantum dots (Kumah et al 2009).

In figure 4 we present as an example the diffraction intensity along the (11̅L) Bragg rod. The blue and red curves represent the experimental data and the diffraction intensity profile obtained using the COBRA-determined electron density, respectively. Note that the two are in very good agreement.

In figure 5 we present the electron densities (EDYs) along two lines normal to the surface going through two different Si atoms in the substrate unit cell. The EDYs along the lines going through the other two Si atoms in the substrate unit cell are similar to the ones presented here. The peaks to
the left of $Z = 0$ correspond to the substrate while the large peaks to the right correspond to the wetting and cap layers. The peaks are larger because these layers contain Ge. The fact that these peaks are large and narrow indicates that the atoms in these layers are well registered with respect to the substrate. The small peaks further to the right correspond to the folded structure of the islands base (Yacoby et al 2000). This means that the atoms in the island’s base are also well registered relative to the substrate. AFM and HRTEM show that the islands are about 11 nm high. This is much larger than the 2 nm height observed in figure 5. The discrepancy is understood by realizing that the atoms in the upper parts of the islands are no longer registered with respect to the substrate. figures 2(b) and (c) show that the layers close to the substrate are planar but relax and bend further up the islands leading to loss of registration. The bending of the atomic layers has also been observed by COBRA in other quantum dot systems (Kumah et al 2009, Yacoby et al 2013).

The detailed HRTEM analysis presented in section 3.1 shows that the unit cells in the islands are displaced relative to the extrapolation of the substrate. Consequently, the atoms in the upper layers of the islands lose registry with respect to the substrate and cannot be seen by COBRA.

Let us now look at the EDY data in more detail. We shall refer to the first peak on the left (figure 5(a)) as the substrate-like peak. Similarly we shall refer to the small broad peak at $Z = 2.6$ nm as an island-like peak. Notice that the four peaks at $Z > 0$ appear to be composed of substrate- and island-like peaks with varying weights. We have fit all EDY peaks along all four lines going through the four different Si atoms in the folded unit cell with a combination of these two types of peaks using the weights as fit parameters. The resulting weights were then multiplied by the integrated electron density of the corresponding peak and are shown in figure 6. These results show that the folded structure EDY in the $0 < Z < 2$ nm range contains both island-like peaks and substrate-like peaks. This is consistent with the step-bunching observed in this system. Due to step-bunching, the surface of the Si substrate is not planar, so the bases of different islands are at different heights in the $Z$-direction and appear to overlap with the continuous film and/or WL.

Using the electron density in figure 5, the displacement of the Si/Ge atoms along one line normal to the surface relative to the corresponding atoms on a substrate-defined reference grid are shown in figure 7 as a function of cell number. The peak positions were determined using the Gaussian positions obtained by fitting the line shapes as discussed in the previous paragraph. The average slope between cell 6 (at the nominal substrate interface) and cell 10 determines the average change in unit cell size. The measured ratio $c/c_{\text{bulk}} = 1.014 \pm 0.004$. This is consistent with a WL composed of only one unit cell out of the 4 having very high Ge concentration so the average unit cell change (1.4%) is, as expected, about one quarter of a $Z$-direction unit cell of a pure Ge film strained laterally to the Si unit cell. We stress that the profiles in figure 5 represent the electron density in the 2D folded unit cell.

Therefore, due to the step bunching, each peak in the electron density profile corresponds to a mixture of Si from the buffer layer, Ge/Si from the WL and Si from the cap layer.

In order to determine the Ge concentration we have carried out energy differential COBRA measurements using anomalous x-ray scattering at the Ge K-edge as a probe (Yacoby et al 2000, Kumah et al 2008). We have measured the difference between the diffraction intensities at two energies at each point along portions of the ten symmetry-inequivalent Bragg rods. One energy was just below the Ge absorption edge (at 11.09 keV) while the other was just above it (at 11.11 keV). To obtain the diffraction intensity difference accurately it is necessary to measure the diffraction intensities at the same point along the Bragg rod with an accuracy of better than $10^{-3}$ deg. This was accomplished by adjusting the sample orientation for each energy, using piezo actuators. The differential diffraction intensity data was analyzed by expressing the calculated diffraction intensity difference in terms of the COBRA determined EDY and treating the Ge concentration in each atomic layer as a variable fit parameter.

**Figure 6.** Integrated electron density as a function distance from the substrate--wetting layer interface at $Z = 0$. Open blue squares denote the film-like component, full red dots the island-like component.

**Figure 7.** The cumulative displacement of the atoms along a line perpendicular to the surface relative to a substrate-defined frame of reference as a function of unit cell number. Cell 6 is the wetting layer--substrate interface and corresponds to $Z = 0$ nm. The slope of the black line between cell 6 and cell 10 determines the average size of the wetting layer/cap layer unit cell.
In the present case the number of fit parameters was 32 corresponding to 8 unit cells in the range $-0.8 < Z < 3.67$ nm. The fits obtained are shown in figure 8. Note that the number of data points is much larger than the number of parameters. The fitting was done using both the ‘fmincon’ MATLAB command that finds the minimum of a constrained nonlinear multivariable function, and the differential evolution method (GenX); both methods converged to the same minimum.

The Ge concentration is shown in figure 9. Using the fit Hessian, and the number of experimental points and the number of parameters, we estimate that the error is $\pm 14\%$. The large peak corresponds to the region where the layers cover the entire surface. We interpret this as the WL. To the right of this peak is a shoulder, indicating that in the range $1.2 < Z < 1.8$ nm the folded structure in each atomic monolayer contains both Si and Ge. As discussed in section 4 this mixture is a result of the step-bunching, causing the signal from the Si of the cap layer and that of Ge in the WL to mix. The minimum in the Ge concentration at $Z = 2.2$ nm occurs because the folded structure is a mixture of the cap Si atoms that cover most of the area and islands that cover only a small fraction of the area. As seen at $Z = 3$ nm, even in planes that contain only islands, the concentration of Ge is only about 30%. Consequently the fraction of Ge atoms close to $Z = 2.2$ nm is significantly diminished.

4. Discussion

In order to understand the determined Ge content as a function of the height above the Si buffer layer, as shown in figure 9, we have to consider (i) the influence of the morphology of the Si buffer layer on the subsequent growth of the Ge-rich WL and of the islands themselves; and (ii) the influence of the loss of registry with increasing height, of the atomic planes in the islands with respect to the Si substrate, due to strain relaxation in the dome-shaped islands.

To obtain more quantitative information on the influence of the step-bunching on the COBRA results, AFM data of the surface morphology are invoked. In addition to the surface undulations stemming from step-bunching, the WL and the dome-shaped islands, trenches are known to form around these types of islands (Kamins et al 1997, Chaparro et al 2000, Kumah et al 2011, Yacoby et al 2013). Figure 10 depicts the height distribution of AFM data pixels, as recorded from an AFM-micrograph of $5 \times 5 \mu m^2$ size. The number of pixels used for the histogram amounts to about 260 000, corresponding to an array of $512 \times 512$ pixels. Since dome-shaped islands are surrounded by trenches that penetrate the WL and expose the Si substrate, the zero level was chosen to be the average depth of the island’s trenches. Consequently, the surface undulations onto which the WL is deposited with a thickness of typically four monolayers, amount to height variations of the order of 1 nm. Thus the region from about $z = 0$ to about 2 nm in figure 9 is attributed to the wetting and cap layers.

The observed shape of the Ge concentration profile is a result of convoluting the actual Ge concentration profile with
the height distribution due to step bunching shown in figure 10. The de-convoluted shape has been obtained by Fourier transforming the observed Ge concentration and the height distribution. The high frequency parts of the Ge concentration Fourier transform are noise-dominated and were filtered out. Then the ratio of the two transforms was calculated and back Fourier transformed to yield the true Ge concentration. This is represented by the solid red curve in figure 9.

Beyond z = 2 nm in figure 9, a region in which the islands themselves contribute to the COBRA signal, we deduce an apparent Ge content close to zero before a further increase of the Ge content prevails. To account for this minimum in the Ge content, one has to bear in mind that following the Ge deposition the surface of the sample is covered by a cap layer of about 2 nm of Si. Due to the rather small areal density of the islands a signal which originates from this Si cap layer actually intermixes with the one from the base of the islands and we estimate that at a height z = 2.3 nm the Ge content averaged over the entire surface would be only about 4%. Within the error bars, this value is in agreement with the results plotted in figure 9. The further increase of the Ge content for Z > 2.3 nm is attributed to the fast rising Ge concentration in the islands. However, beyond z = 3 nm the electron density drops and the Ge concentration is no longer reliable. We attribute this drop as being caused by the rather large size of the dome shaped islands and the concomitant relaxation both along the growth direction, as well as laterally, as evidenced from the HRTM data and their DALI analysis. As outlined above, towards the apex of the island, the relaxation along the [001] growth direction amounts to more than one Si (002) plane distance as is evident from figure 2. Along the lateral direction, the relaxation at the side facets is on the order of one Si (002) interplanar distance. Thus a close inspection and analysis of figure 2(a) reveals that within the islands, both towards the apex as well as towards the side facets the relaxation is too large to maintain good coherence with the substrate. Thus, registry of the atoms in the islands with respect to the ones in the substrate is lost and the COBRA analysis breaks down. We therefore conclude that the COBRA method is suitable for the compositional analysis of sufficiently small SiGe islands such as hut clusters and pyramids but is not suitable for large islands like domes and barns. Furthermore, using an amorphous cap layer, and avoiding a thick buffer layer to minimize step-bunching, will simplify the interpretation of the COBRA results.

It is interesting to compare the atomic structure of this system with the Ge/Si system investigated previously (Yacoby et al 2013). The growth procedure of the two systems is quite different. They differ in three important respects: first, the base diameter of the present islands is about 4–5 times larger than that of the samples described in (Yacoby et al 2013); second, the island density is much smaller here (5.7 x 10^7 cm^-2 for the domes and 3.8 x 10^6 cm^-2 for the pyramids) compared to 3 x 10^11 cm^-2 in (Yacoby et al 2013); and third, the height of the present islands is also larger, 11 nm as compared to 3–6 nm. The fact that the present islands are much larger both in base diameter and in height explains why the atoms in the present islands are not in complete registry with the Si atoms in the substrate. Consequently, in spite of the fact that the height of the present islands is larger, the number of monolayers that COBRA identifies is much smaller. The present islands have been grown on a 45 nm Si buffer layer. As explained above, due to step-bunching the resulting surface is not flat. This shows up as overlap of the islands and the WL as seen in figures 4 and 5. In contrast, in (Kumah et al 2011) the surface is atomically flat with very small roughness, in which case the EDYs of the islands and the WL do not overlap. In spite of the differences in the growth conditions, the Z dependences of the Ge concentration are quite similar with the exception of the shoulder at 1.2 < Z < 1.8 nm. As pointed out above, the shoulder is probably a result of the step-bunching present in this system and absent in the system reported in (Kumah et al 2011).

5. Summary

A structural and compositional analysis has been performed on the Ge WL and islands grown by molecular beam epitaxy on (001) Si substrates. We studied the structure and composition distribution in the WL and the islands using a combination of three techniques: AFM, high resolution transmission electron microscopy and the differential COBRA. The Ge content and distribution in the WL has been established and a rather high Ge content, in excess of 80%, has been determined. For the formation of nanostructures from supersaturated WLs this high Ge content is of utmost importance, as the chemical composition directly influences the surface kinetics, crucial for the formation of homogeneous islands, defect-free in-plane nanowires and ordered quantum dots and quantum dot molecules of arbitrary density (Zhang et al 2015). Our results resolve a long-standing debate about the WL composition since previously both high, as well as rather low, Ge contents were reported in the literature. The Ge profile and the maximum Ge content reported in this work are in agreement with data obtained from the analysis of photoluminescence experiments using model calculations. However, we stress that here the results are obtained by direct structural characterization independent of simulations on the influence of size quantization on the electronic structure of the WL. As far as the islands are concerned, information obtained from the COBRA method on the Ge concentration gradient in large dome-shaped islands with large lattice mismatch is limited to only the first few unit cells above the substrate/WL interface. Beyond this height, the strain relaxation in dome shaped islands is dominant due to their steeper facets as compared to those of hut clusters and pyramids, and consequently registry with the atomic positions in the reference Si substrate lattice is lost.
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