Surfactant adsorption site and growth mechanism of Ge- on Ga-terminated Si(111)

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X-ray standing waves have been employed to study the microscopic mechanism of surfactant mediated epitaxy of Ge on Si(111). After deposition of 0.5 BL Ge on the Ga:Si(111)-6.3×6.3 surface we find Ga floating on the surface in a Ga-Ge bilayer with Ga in a substitutional adsorption site. Deposition of 0.5 BL Ge on the Ga:Si(111)-$\sqrt{3}\times\sqrt{3}$ surface leads to a change of the Ga adsorption site from T_4 to substitutional and the formation of very small 6.3×6.3 domains with a local Ga coverage of 0.8 ML. Since the average Ga coverage of the $\sqrt{3}\times\sqrt{3}$ surface is 0.33 ML only, the change of adsorption site is accompanied by the formation of locally Ga free surface areas in coexistence with the 6.3×6.3 domains. Thus, further Ge deposition on this surface leads to the formation of Ge islands of a uniform height. [S0163-1829(96)51148-3]

Since its discovery[1] in 1989 surfactant mediated epitaxy has received considerable attention due to its capability of altering the growth mode of Ge on Si from layer by layer growth for the first two bilayers followed by islanding (Stranski-Krastanov growth) to growth of a homogeneous Ge film of uniform thickness.[2–10] Surfactants in this context are atoms which form surface active species. Among the list of surfactants Ga is of particular scientific interest since it can be used to study the effect of surface reconstruction and surfactant coverage on epitaxial growth in a well-defined manner.[6]

Adsorption of Ga on Si(111) leads to the formation of two distinct surface reconstructions,[11] as shown in Fig. 1. At a surface Ga coverage of 1/3 ML a $\sqrt{3}\times\sqrt{3}$ reconstruction is formed with Ga residing in a T_4 site. At higher Ga coverages a discommensurate 6.3×6.3 reconstruction with a saturation coverage of ~ 0.8 ML is found with Ga in a substitutional site in the upper half of the surface bilayer. It has been shown that the Ga coverage determines whether or not Ga acts as surfactant for Ge growth on Si(111).[6] The Ga:Si(111)-6.3×6.3 surface has been shown to be an active surfactant. Ge deposition onto the 6.3×6.3-terminated Si(111) surface results in Ge films of uniform thickness, while growth of Ge on $\sqrt{3}\times\sqrt{3}$-terminated Si leads to islanding of the deposited Ge. Hence the Ga/Si(111) system enables both the impact of surface coverage and surface reconstruction on heteroepitaxial growth to be studied. This paper will focus on the aspect of the adsorption site geometry of the surfactant and Ge during growth. We therefore employed x-ray standing waves (XSW's), which provide a high spatial resolution (0.03 Å in this case).

Sample preparation was performed in an ultrahigh vacuum (UHV) system with a base pressure of 3×10^{-11} mbar. After chemical cleaning (RCA) Si(111)-7×7 substrates were prepared by annealing at 900 °C for 10 min. Ga and Ge were evaporated from Knudsen cells at a substrate temperature of 470 °C and a deposition rate of 0.2–0.4 ML/min [1 monolayer (ML)=7.83×10^{14} cm^{-2}; 1 bilayer (BL) =2ML]. The deposition rate was measured with a quartz balance. The final coverage was checked by x-ray fluorescence measurements. We estimate the accuracy of the given

coverages to ±20%. Sample preparation and growth was monitored by reflection high-energy electron diffraction (RHEED) and Auger electron spectroscopy (AES). Ga deposition at 470 °C. resulted in a streaky 6.3×6.3 RHEED pattern. For preparation of the Ga:Si(111)-$\sqrt{3}\times\sqrt{3}$ surface further annealing at 670 °C for 5 min was applied. This leads to partial desorption of surface Ga and the formation of a $\sqrt{3}\times\sqrt{3}$ surface reconstruction. This procedure resulted in a sharp $\sqrt{3}\times\sqrt{3}R30°$ RHEED pattern. The preparation of Ga-terminated substrates was followed by deposition of ~ 0.5 BL Ge. During growth a pressure better than 1×10^{-9} mbar was maintained. After preparation the samples were transferred into a portable UHV chamber, equipped with a hemispherical Be window for x-ray measurements and a base pressure better than 1×10^{-9} mbar. XSW measurements in (111) and (220) reflection were performed consecutively on the same sample after each preparation.

X-ray standing waves measurements were performed at the HASYLAB bending magnet beamline ROEMO I. For XSW a standard nondispersive setup with a monochromator consisting of a symmetric and an asymmetric Si crystal was used at a photon energy of 12.5 keV, employing (111) and (220) crystals for XSW measurement in (111) and (220) Bragg reflection, respectively. The rocking curve and Ga and Ge K$_\alpha$ fluorescence yield were monitored simultaneously by repetitively sweeping the incidence angle through the Bragg condition. The coherent position and the coherent fraction of Ga and Ge were determined from the data by fitting reflectivity and fluorescence to expressions derived from the dynamical theory of x-ray diffraction.[12,13]

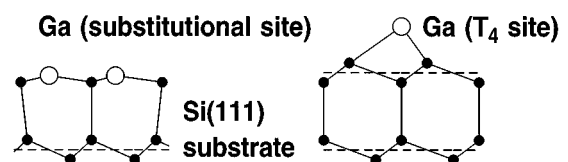The coherent position Φ_A^{hkl} and the coherent fraction

FIG. 1. Adsorption site geometry of Ga on Si(111) in the 6.3×6.3 (substitutional) and $\sqrt{3}\times\sqrt{3}$ (T_4) reconstruction.
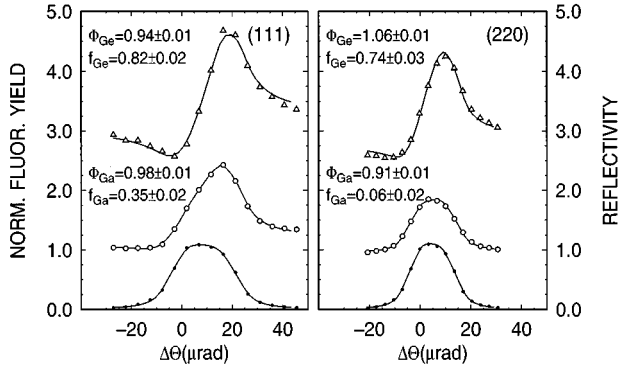
FIG. 2. Ge K_α fluorescence yield ($\triangle$), Ga K_α fluorescence yield ($\bigcirc$) and reflectivity ($\bullet$) in (111) and (220) Bragg reflection (upper and lower curves, respectively) after deposition of 0.5 BL Ge on Ga:Si(111)-6.3×6.3 at 470 °C. The Ge fluorescence has been shifted by 2 for display purposes.

FIG. 3. Schematic diagram indicating the atomic positions in the Ge film after deposition of Ge on Ga:Si(111)-6.3×6.3.

f_A^{hkl} are the phase and amplitude, respectively, of the (hkl) Fourier component of the atomic distribution function[14] with (hkl) denoting the diffraction planes employed for Bragg reflection and A denoting the element. Details of the analysis can be found in the literature.[15,16]

From the literature, the coherent position of Ga in the 6.3×6.3 reconstruction is known to be $\Phi_{Ga}^{111} = 0.97$.[11] Figure 2 shows the Ga K_α fluorescence yield, the Ge K_α fluorescence yield and the reflectivity in (111) and (220) Bragg reflection after deposition of $\sim$ 0.5 BL Ge on Ga:Si(111)-6.3×6.3. Employing the (111) Bragg reflection for XSW measurements, a coherent Ga position of $\Phi_{Ga}^{111} = 0.98 \pm 0.01$ is found. This is consistent with Ga in a substitutional site. From previous experiments it is known that Ga floats on the surface during Ge deposition on Ga:Si(111)-6.3×6.3.[6] From our XSW results we conclude that Ga floats on the surface and forms a surface bilayer with Ga in the upper and Ge in the lower level of the surface bilayer, similar to Ga and Si in the 6.3×6.3 reconstructed starting surface. The coherent fraction $f_{Ga}^{111} = 0.35 \pm 0.02$ is significantly reduced when compared to a perfect Ga:Si(111)-6.3×6.3 surface and we attribute this to excess Ga atoms which accumulate on the surface. In (220) Bragg reflection the coherent Ga fraction is very low. Together with the larger coherent Ga fraction in (111) reflection this indicates the existence of a discommensurate surface reconstruction. If the domains of a discommensurate reconstruction are large compared to its quasi periodicity then the corresponding coherent fraction must vanish. We observe a value of $f_{Ga}^{220} = 0.06 \pm 0.02$, which is small but distinct from 0. Thus we conclude that the domain size is in the order of some unit cells of the reconstruction. This is also supported by a diffuse 6.3×6.3-like RHEED pattern, observed after Ge deposition. A quantitative analysis of the lateral structure within the domains strongly depends on details of domain size, shape and structural parameters and will thus not be performed here. Microscopical measurements will be very interesting in order to address this question. Our observations are in agreement with previously published investigations showing that Ga adsorption on Ge(111) also leads to the formation of a discommensurate reconstruction.[17,18]
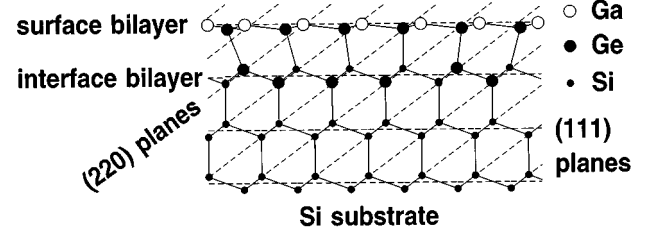
The Ge fluorescence yield in (111) and (220) Bragg reflection is displayed in Fig. 2. For XSW measurements on perfect crystals with a diamond structure, a coherent position of $\Phi_c = 1$ and a coherent fraction of $f_c = 0.7$ will be observed due to the equal occupancy of the upper and lower levels of the (111) bilayers. After deposition of 0.5 BL Ge on the 6.3×6.3 surface, we find a coherent Ge position $\Phi_{Ge}^{111} = 0.94 \pm 0.01$ and a coherent Ge fraction $f_{Ge}^{111} = 0.82 \pm 0.02$. From the XSW measurements for Ga we concluded on the formation of a Ga-Ge surface bilayer, similar to the Ga-Si surface bilayer in the case of the Ga:Si(111)-6.3×6.3. Ga occupation of the on-top position is not compatible with the Ga XSW results. Thus, in the most simple view of the initial growth process, Ge deposition leads to a replacement of the Ga in the upper level of the substrate surface bilayer by Ge and the formation of a Ga-Ge surface bilayer on the newly formed Ge-Si interface bilayer.

We have used this model as a starting point and calculated the coherent position and fraction for Ge, taking into account a pseudomorphically strained structure as schematically shown in Fig. 3 with a vertical expansion of 2–3 %. In a first approach we tried to model the XSW results allowing a contraction of the vertical spacing between the Ga-Ge surface bilayer. Within the boundaries for pseudomorphic growth, it was not possible to find a structure that yields agreement with the measured coherent Ge position of $\Phi_{Ge}^{111} = 0.94$ *and* the large coherent Ge fraction of $f_{Ge}^{111} = 0.82$, unless a substantial fraction of the interfacial Ge exchanges site with underlying Si. Agreement with the data can be found if 50–70% of the Ge resides in the lower level of the interface bilayer. This value is rather independent of the Ge bond length between Ge in the Ga-Ge surface bilayer and Si or Ge in the underlying Ge-Si interface bilayer. The given range represents a variation of this parameter between 2.32 Å and 2.52 Å. For comparison, bulk Ge shows a value of 2.45 Å. The conclusion on interfacial intermixing is supported by recent studies using high-resolution photoemission spectroscopy that also show substantial Ge-Si intermixing for MBE and SME grown Ge films on Si(001).[19]

The incorporation of Si into the Ga-Ge surface bilayer or intermixing of Ge and Si in bilayers below the interface have not been accounted for in the calculation. Nevertheless, we regard these processes to be additionally possible. Here, we like to point out that these would increase the Ge amount in the upper levels of the (111) bilayers and thus further increase the calculated probabilities for Ge-Si site exchanges. The large amount of intermixing between Ge and Si at the interface may be understood in terms of interface stress which is due to the difference in lattice constant between Si
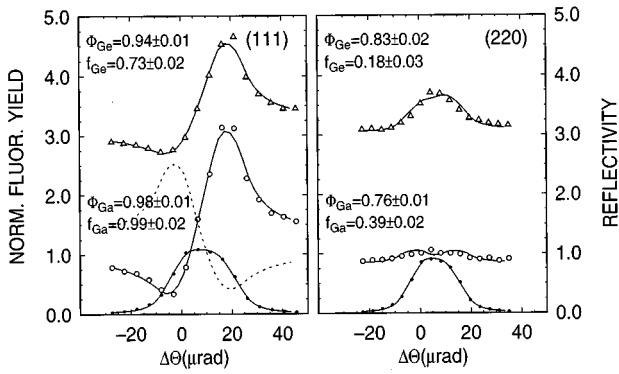
FIG. 4. Ge K_α fluorescence yield ($\triangle$), Ga K_α fluorescence yield ($\bigcirc$) and reflectivity ($\bullet$) in (111) and (220) Bragg reflection (upper and lower curves, respectively) after deposition of 0.5 BL Ge on Ga:Si(111)-$\sqrt{3} \times \sqrt{3}$ at 470 °C. The dashed curve shows the Ga fluorescence yield of the initial Ga:Si(111)-$\sqrt{3} \times \sqrt{3}$ surface prior to Ge deposition (Ga in T_4 adsorption site). The Ge fluorescence has been shifted by 2 for display purposes.

and Ge. An abrupt interface is not stable and the system lowers its total stress by extending the interface over more than one atomic plane.

We now turn to the evaluation of the measurements for Ge in (220) Bragg reflection. We measure a coherent Ge fraction of $f_{Ge}^{220} = 0.74 \pm 0.03$. For a perfect Ge film a value of $f_{Ge}^{220} = 0.97$ is expected. The reduced value can be attributed either to the involvement of Ge in a discommensurate Ga-Ge surface bilayer or the existence of stacking faults which has been reported from transmission electron microscopy (TEM) measurements.[6] In (220) reflection we find a coherent Ge position of $\Phi_{Ge}^{220} = 1.06 \pm 0.01$, which can be understood by the presence of strain in the Ge-Si layers. The result corresponds to a vertical expansion of the Ge-Si layers of 3%. This is consistent with the values used previously for the model calculations. In (220) reflection the coherent fraction for Ge is larger than for Ga. We find $f_{Ge}^{220} = 0.74 \pm 0.03$ in comparison to $f_{Ga}^{220} = 0.06 \pm 0.02$. The larger coherent Ge fraction is due to the small size of the 6.3×6.3-like domains and the Ge atoms in the interface and deeper bilayers. These are not discommensurate but well ordered with respect to the (220) diffraction planes and give rise to a high coherent fraction.

While the Ga terminated 6.3×6.3 surface successfully acts as a surfactant for Ge heteroepitaxy, it has been shown by medium-energy ion-scattering (MEIS) that the $\sqrt{3} \times \sqrt{3}$ does not promote layer by layer growth. Instead, Ge islands of uniform thickness are formed and, interestingly, the height of the islands is much more uniform than is the case for growth without Ga.[6] In the following we will address the question on the underlying mechanism. As schematically shown in Fig. 1, Ga occupies a T_4 surface site in the Ga:Si(111)-$\sqrt{3} \times \sqrt{3}$ reconstruction. From the literature, the coherent Ga position for this structure is known to be[11] $\Phi_{Ga}^{111} = 0.59$ (dashed curve in Fig. 4). This value was also confirmed in our control experiments.

Figure 4 shows the Ga K_α fluorescence yield, the Ge K_α fluorescence yield and the reflectivity in (111) and (220) Bragg reflection after deposition of 0.5 BL Ge on the $\sqrt{3}$

$\times \sqrt{3}$ surface. We find a coherent Ga position of $\Phi_{Ga}^{111} = 0.98 \pm 0.01$ and a coherent Ga fraction of $f_{Ga}^{111} = 0.99 \pm 0.02$. The coherent Ga position is identical to the one found for Ga in the 6.3×6.3 reconstruction. Thus we conclude that during Ge growth Ga changes its adsorption site from T_4 to substitutional. There are two possibilities to explain the data. Either the Ga forms 6.3×6.3-like domains with Ga-Si surface bilayers with no Ge involved or a Ga-Ge surface bilayer is formed. From XSW it is not possible to distinguish between both possibilities.[20] Any mixture of the two models is also possible. The change of adsorption site is accompanied by a local change of the surface periodicity, which is also visible in RHEED. Before Ge deposition, a sharp $\sqrt{3} \times \sqrt{3}$ RHEED pattern is observed and after Ge deposition a very diffuse 6.3×6.3-like pattern is found. The formation of 6.3×6.3 domains requires a local Ga coverage of 0.8 ML. As the average Ga coverage of the surface is only 0.33 ML, the result of the process described above is a surface that is partially covered with small 6.3×6.3 domains and patches of Ga-free areas.

Apparently the T_4 adsorption site is not favorable for Ga on strained Ge/Si(111) in agreement with studies on Ga adsorption on Ge(111).[21] MEIS data show that approximately 2/3 of the surface is covered with Ge islands.[6] The average Ga coverage of the surface is 0.33 ML. Since the 6.3×6.3 structure requires a local Ga coverage of 0.8 ML, the integral surface area covered by 6.3×6.3 domains is smaller than the integral surface area that is free of Ga. Thus we regard it most likely that Ge nucleation takes place in those surface areas that are not covered with Ga. This is supported by the coherent Ga fraction of $f_{Ga}^{111} = 0.99 \pm 0.02$ found for this surface. From MEIS measurements it is known that the Ge islands have a height distribution. The Ge islands have a different vertical spacing than the Si substrate. Thus, if the Ga was residing on top of the islands, the coherent Ga fraction would be significantly smaller due to Ga in different Ge ''levels'' with respect to the substrate.

This conclusion is also in agreement with previous studies that found an enhanced surface diffusion of Si and Ge after adsorption of group-III elements on Si(111).[10] The enhanced diffusion results in a transport of Ge to surface areas that locally are not covered with Ga where Ge islands nucleate. As mentioned above, the height distribution of the Ge islands is more sharply peaked than that found for Stranski-Krastanov growth on bare Si.[6] This can be explained by nucleation conditions that are more homogeneous due to the decay process of the $\sqrt{3} \times \sqrt{3}$ reconstruction. This process results in a patchwork of surface areas that are free of Ga and get overgrown by Ge islands with further Ge deposition. The coherent Ga fraction measured in (220) Bragg reflection of $f_{Ga}^{220} = 0.39 \pm 0.02$ (Fig. 4) is large in comparison to the value for the Ga:Si(111)-6.3×6.3 and after Ge growth on this surface. For the Ga:Si(111)-6.3×6.3 a vanishing f_{Ga}^{220} value has been reported.[11] And after Ge growth on this surface we measured a coherent Ga fraction of $f_{Ga}^{220} = 0.06 \pm 0.02$. Taking into account the presence of disordered excess Ga known from the (111) results, one calculates a scaled coherent Ga fraction of $f_{Ga}^{220} \sim 0.17$. We attribute the larger coherent fraction to the existence of small 6.3×6.3-like domains on the surface as confirmed by the observation of a diffuse RHEED

pattern. If the domains ''lock in'' at a certain surface site with respect to the surface, and the size of the domains is not large compared to its surface periodicity, then the Ga distribution is not truly random with respect to the (220) diffraction planes. This results in a nonvanishing value of the coherent Ga fraction.

The XSW data for Ge after growth of 0.5 BL on Ga:Si(111)-$\sqrt{3} \times \sqrt{3}$ are displayed in Fig. 4. In (111) Bragg reflection we find a coherent Ge position of $\Phi_{Ge}^{111} = 0.94 \pm 0.01$ and a coherent Ge fraction of $f_{Ge}^{111} = 0.73 \pm 0.02$. The interpretation of these values strongly depends on the surface morphology. However, the value of $\Phi_{Ge}^{111} < 1$ may be interpreted as an indication of intermixing of Ge and Si at the interface as discussed previously for growth on Ga:Si(111)-6.3×6.3 substrates. The coherent Ge fraction in (220) Bragg reflection is determined to $f_{Ge}^{220} = 0.18 \pm 0.03$. This value is smaller than found for Ga on the same surface. Hence, Ge incorporation into a 6.3×6.3 like surface reconstruction is not sufficient to explain this result. However, it can be explained by the existence of stacking faults in a significant fraction of the Ge islands, as found after growth on[6] the Ga:Si(111)-6.3×6.3 by TEM and MEIS.

Previously we assumed that nucleation of Ge islands on this surface takes place in those surface areas that are free of Ga. In this case the origin of the stacking faults must be different from the origin of stacking faults found after Ge growth on the Ga:Si(111)-6.3×6.3. However, we strongly suggest further investigations of the system with microscopical methods, such as scanning tunneling microscopy (STM) or low-energy electron microscopy (LEEM) for clarification of this point.

In conclusion, we have shown that Ga maintains a discommensurate reconstruction during Ge growth on the Ga:Si(111)-6.3×6.3 surface, with Ga residing in a substitutional adsorption site. During Ge growth Ga floats on the surface and successfully acts as surfactant. The Ga:Si(111)-$\sqrt{3} \times \sqrt{3}$ surface fails as surfactant due to a change of adsorption site of Ga during Ge deposition. The $\sqrt{3} \times \sqrt{3}$ reconstruction decays into a surface locally consisting of small 6.3×6.3 like domains and Ga free areas in coexistence. Further growth of Ge on this surface leads to formation of Ge islands with a narrow height distribution.

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