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Evolution of the strain relaxation in a Ge layer on Si(001) by reconstruction and intermixing

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The periodicity of the $(2\times N)$ reconstruction of two-dimensional Ge layers on Si(001) is measured as a function of the Ge coverage with a high-temperature scanning tunneling microscope during growth. The strain energy, which increases with increasing coverage, is the driving force for the formation of the strain relieving $(2\times N)$ reconstruction trenches and Si/Ge intermixing. A quantitative comparison to total-energy calculations predicting the periodicity of the $(2\times N)$ reconstruction with the experimental results is used to estimate the amount of Si-Ge intermixing near the surface. [S0163-1829(99)50528-6]

In many lattice mismatched heteroepitaxial systems the Stranski-Krastanow growth mode is observed. This growth mode consists initially of the formation of a two-dimensional (2D) pseudomorphic strained layer. During the growth of thicker layers, the increasing misfit strain leads to a transition to different growth morphologies: The formation of coherent, dislocation-free 3D islands or the formation of misfit dislocations are efficient ways of relieving the misfit strain partially. Besides this transition to different growth morphologies during the later stages of growth, even during the formation of the inital 2D layer, the surface reconstruction may change to accommodate for the increasing strain energy.

In the case of Ge epitaxy on Si(001), a $(2\times N)$ reconstruction is observed on the two-dimensional strained layer (wetting layer).[1–3] This reconstruction consists of a periodic array of missing dimers of the (2×1) dimer reconstruction. Every Nth dimer of the (2×1) reconstruction is missing. In the STM (scanning tunneling microscope) images [Figs. 1(b)–(d)] dark lines are visible, which correspond to rows of aligned missing dimers. A schematic top view of the $(2\times N)$ reconstruction is represented in the inset of Fig. 2. This regular array of trenches is an effective way to reduce the misfit strain partially by outward relaxation of the Ge near the trenches. On the other hand, the formation energy of the trenches leads to an increase of the film energy. The balance between these two driving forces determines the periodicity of the reconstruction. Additionally, the reconstruction periodicity (N) is dependent on the stoichiometry of the wetting layer, i.e., the amount of Si/Ge intermixing, which is still difficult to determine, despite extensive studies of this surface.

Total-energy calculations based on empirical potentials were used to predict the periodicity of the $(2\times N)$ reconstruction[4,5] as a function of Ge coverage and as a function of the intermixing between Si and Ge. Different experiments determining the periodicity N of the $(2\times N)$ reconstruction were performed under various conditions.[1–3,6–8] This makes a consistent comparison with the theoretical models difficult.

Here, we present direct STM measurements of the periodicity N of the reconstruction performed continuously as a function of the Ge coverage. The STM measurements are performed at high temperature during deposition of Ge. The observed decrease in the reconstruction periodicity is compared to predictions of total-energy calculations by Feng Liu *et al.*[5] A quantitative agreement of the observed periodicity with the calculations is obtained for Si intermixing of 12% in the Ge wetting layer.

The experiments were carried out with a high-temperature STM, in which the growing surface is imaged continuously during growth. We used a beetle-type STM, which is described in detail in Ref. 9. The molecular beam from a Ge evaporator is directed towards the sample, which is located in the STM position. Evaporation is done continuously while the STM is scanning the growing film. This results in sequences of images (movies) showing the growth behavior. Ge is evaporated from an electron-beam evaporator. The STM measurements were performed in an ultrahigh vacuum chamber (base pressure 3×10^{-11} mbar). We used a sample

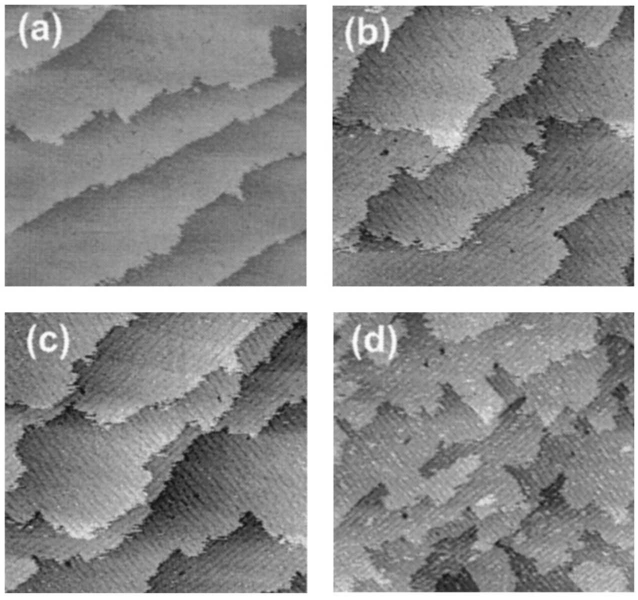

FIG. 1. Sample images from a growth movie showing the wetting layer growth of Ge on Si(001) and the evolution of the $(2\times N)$ surface reconstruction [image area: 1600×1500 Å^2, $T=575$ K, Ge coverages: 0, 0.92, 1.26, 1.82 Ml in (a) to (d), respectively]. The distance between the trenches of the $(2\times N)$ reconstruction decreases with coverage. The complete growth sequence is available as a movie on the World Wide Web: http://www.fz-juelich.de/video/voigtlaender/.

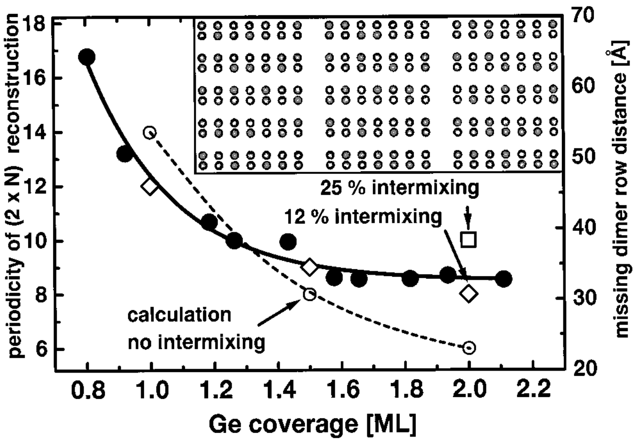

FIG. 2. Periodicity (N) of the ($2\times N$) reconstruction as function of Ge coverage on Si(001). The solid circles represent the experimental data showing the trend towards smaller periodicity for increasing coverages. The solid line is a fit to the data to guide the eye. Total-energy calculations without taking into account a possible intermixing (Ref. 5) are displayed as open circles (connected by a dashed line to guide the eye). The open diamonds and the open square represent total-energy calculations taking into account an Si/Ge intermixing of 12% and 25%, respectively. The inset shows a schematic top view of the ($2\times N$) reconstructed surface of Ge on Si(001). Only the top dimers are shown. The trenches of the ($2\times N$) reconstruction (perpendicular to the dimer rows) are formed by removal of every Nth dimer.

bias voltage of +2 V and a tunneling current of 300 pA.

Figure 1 shows sample images of a growth movie taken during the growth of the Ge wetting layer on Si(001) ($T=573$ K, growth rate: 0.05 Ml/min ($1\text{ Ml}=6.78\times 10^{14}$ atoms/cm^2), image area 1600 Å $\times$1500 Å). The observed growth mode during the formation of the Ge wetting layer is initially apparently step-flow growth, i.e., the steps are observed to move and no formation of 2D islands is observed. Starting at a coverage of about 0.3 Ml, missing dimers begin to align in form of rows, forming trenches. As well as the dimer rows of the (2×1) reconstruction, the trenches also change their direction by 90° for two terraces separated by a step. For coverages higher than 0.7 Ml the trenches form a regular array with quite a regular spacing between the trenches. With increasing coverage the distance between the trenches is observed to decrease.

As can be seen, for instance, in Fig. 1(b), the formation of the ($2\times N$) reconstruction is observed with the same spacing at all locations on the surface, even for submonolayer coverage. This is not what would be expected for step flow growth of Ge. In this case one would expect to observe domains of ($2\times N$) reconstruction near the preexisting step edges (where the Ge would be expected to be incorporated) and no ($2\times N$) reconstruction in the areas which are not covered by Ge. The uniform occurrence of the ($2\times N$) reconstruction shows that the incorporation of Ge does not occur at the step edges. The deposited Ge atoms diffuse over the surface and are incorporated by exchanging places with Si atoms on the terraces. The displaced Si atoms diffuse to the step edges and are incorporated there. This so-called displacive incorporation was proposed previously.[7,10] If the chemical identity of the atoms is unknown, this looks like step flow growth. The displacive incorporation of Ge distributed randomly over the surface is a means of stress relief. Due to the displacive incorporation of Ge, the strain is shared between Si and Ge at submonolayer coverages. The strain energy, which is quadratic in strain, is substantially lower in the case of a mixed Si/Ge layer compared to the case of separate, coexisting domains of Si and Ge.[7]

The reduction of the distance between the trenches formed by missing dimers is visible in the sample images (Fig. 1). In Fig. 2 the averaged distance between the trenches and the corresponding periodicity (N) are plotted as a function of coverage. The measured data are shown as solid circles. The ($2\times N$) periodicity N decreases from 17 at 0.8 Ml rapidly to $N=10$ at 1.2 Ml Ge coverage. For higher coverages, the decrease is slower approaching $N=8-9$ at 2 Ml coverage. The solid curve is a spline to guide the eye.

Before comparing the experimental data for the periodicity of the ($2\times N$) reconstruction as a function of coverage to the results of total-energy calculations,[5] we first introduce a simple model, which elucidates the mechanisms for the formation of the ($2\times N$) reconstruction and its evolution with coverage. In this model, we decompose the energy of the ($2\times N$) reconstructed Ge film on Si(001) [relative to the reference case of a (2×1) reconstructed film] into a part accounting for the misfit strain due to the 4% lattice mismatch between Si and Ge and into a part accounting for the formation of the trenches. These two contributions are of opposite nature. The relaxation of strain energy by allowing for an outward expansion of the strained Ge layer towards the free space created by the trench reduces the energy of the film. On the other hand, the formation of a trench by removing dimers costs extra energy.

To estimate the contribution of the strain relaxation energy, we use the one dimensional model of a Frenkel-Kontorova chain.[11] This model describes a linear chain of harmonically coupled atoms. The coupling of this chain of atoms to the underlying film is modeled by a sinusoidal potential well. Therefore, we consider now one monolayer of Ge on a Si(001) surface. A row of ($N-1$) dimers is coupled in a Frenkel-Kontorova chain. The energy of such a chain is taken from Ref. 11. From this, the strain energy per unit area a^2 ($a=3.84$ Å) of the ($2\times N$) reconstruction is calculated. In Fig. 3 this strain energy (E_{strain}) is plotted as circles. For small N (i.e., a dense array of trenches), the strain energy decreases substantially by outward relaxation at the trenches. For larger periodicities (N) the strain relaxation in the inner parts of the ($2\times N$) rows is less efficient.

While the misfit strain energy is reduced by formation of the ($2\times N$) reconstruction, the removal of surface dimers for the creation of the trenches increases the energy of the film.[12] To evaluate this trench formation energy, we consider the case of an unstrained Ge(001) surface where no contribution of misfit stress is present. The energy for the formation of the ($2\times N$) reconstruction on this surface was evaluated by Tersoff[4] and is plotted in Fig. 3 as triangles. In the first approximation, the energy of the formation of a unit length of a trench is a constant. Therefore the trench formation energy per unit area (E_{trench}) is proportional to $1/N$.

The total energy of the ($2\times N$) reconstructed film is the sum of trench formation energy (E_{trench}) and strain relaxation energy (E_{strain}), shown as squares in Fig. 3. Due to the

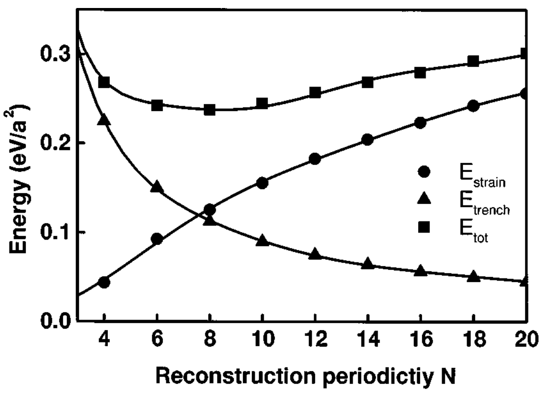

FIG. 3. Different contributions to the energy of a 1 Ml Ge layer forming a $(2\times N)$ reconstruction per unit area as function of periodicity length N. The strain energy calculated from a Frenkel-Kontorova model (Ref. 11) increases with N (circles). The trench formation energy (taken from Ref. 4) decreases proportional to $1/N$ (triangles). The total energy, the sum of both contributions (squares), shows a minimum at $N=8$.

increase of the strain energy with increasing periodicity (N) and a decrease of the trench formation energy with increasing N, a minimum in the total energy results around $N=8$ for a coverage of 1 Ml. Moreover, also the dependence of the $(2\times N)$ periodicity on the coverage can be explained within our simple model as follows: While the trench formation energy should not change much as a function of coverage, the absolute value of the strain energy should increase with increasing Ge coverage below 1 Ml (increasing misfit strain with increasing Ge coverage). In the framework of our model, we can account for this coverage-dependent strain energy by multiplying the strain energy for 1 ML coverage by a coverage-dependent factor. This factor increases from 0 for the clean silicon surface to 1 for 1 ML Ge. Since (E_{trench}) is approximately constant, this results in a shift of the minimum in the total energy ($E_{trench}+E_{strain}$) towards smaller values of N for higher coverages in accord with the experimental results. For coverages above 1 Ml the trenches, which are only 1 Ml deep, do not contribute much to the strain relaxation in the second layer. Therefore, the strain energy increases only slowly for coverages above 1 Ml, resulting in a slow decrease of the periodicity N with coverage. Detailed predictions are beyond the scope of this simple model.

After having discussed the mechanisms for the formation of the $(2\times N)$ reconstruction and the qualitative dependence on coverage, we turn now to a quantitative comparison of the experimental data to total-energy calculations. Feng Liu and Lagally[5] predicted values of $N=14$, 8, and 6 for Ge coverages of 1, 1.5, and 2 Ml, respectively, which are shown in Fig. 2 as open circles. These values do not correspond very well to the experimental data, especially at 2 Ml coverage, where the calculated periodicity ($N=6$) is significantly below the observed value of 8–9. This is the case because in these calculations no Ge/Si intermixing was considered. In several previous experiments indications for a Si/Ge intermixing in the 2D layer were obtained, but it was difficult to quantify the amount of intermixing.[13,14] For the total-energy calculations, all deposited Ge atoms are placed in the top layers. When a certain amount of intermixing is considered at a coverage of 2 Ml, the periodicity of the $(2\times N)$ reconstruction increases. More Si/Ge intermixing causes a reduction of strain energy leading to fewer trenches. Assuming 25% and 12% of Ge segregate from the second layer to the third and fourth, values of $N=10$ and $N=8$ are calculated, respectively.[5] The calculated periodicities for the case of an intermixing of 12% are shown in Fig. 2 as open diamonds for different coverages[15] and correspond very well to the measured data. For the case of 1 Ml coverage the exchange of Ge is not energetically favorable because of the low Ge surface energy. Entropy, however, can drive some Ge from the first to the second layer. For the calculations at 1 Ml coverage, the periodicity ($N=12$) decreased, compared to the case of no intermixing ($N=14$). The total-energy calculations can explain this behavior.[15] The $(2\times N)$ reconstruction leads to a slight tensile stress in the first layer and to a large compressive stress in the second layer.[5] So, allowing some mixing of Ge from the first layer to second layer, the whole surface stress will change toward high compression. Consequently, this leads to lower N value, i.e., more dimer vacancies to relieve this compression. By the quantitative comparison of the measured $(2\times N)$ periodicity as a function of coverage to the predictions of total-energy calculations, the subsurface stoichiometry can be estimated. A Ge intermixing of about 12% provides a consistent match between experiment and theory over a wide range of coverages.

In the later stages of growth beyond 1.8 Ml we observe nucleation of 2D islands besides the previously observed step flow growth [Fig. 1(d)]. We explain this as follows: Due to the increasing strain in the 2D layer, the bonding at the step edges becomes more and more unfavorable, which leads to an increased adatom density and finally to the nucleation of 2D islands. This as a further means of stress relief. Beyond a coverage of 2 Ml, the formation of trenches consisting of missing dimer rows [perpendicular to the $(2\times N)$ trenches] occurs.[1,8] This is another mechanism of stress relief, in this case in the direction perpendicular to the dimer rows.

In conclusion, strain relaxation mechanisms have been studied using STM measurements during the formation of the two-dimensional Stranski-Krastanow layer. The surface reconstruction modifies to allow for a stress relaxation of the strained Ge layer. In particular, the measurement of the evolution of the periodicity of the $(2\times N)$ reconstruction as a function of coverage and the comparison of these data to the results of total-energy calculations results in an intermixing of 12% between Si and Ge.

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