

Si nanostripe formation on vicinal Ge(100) surfaces

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Abstract

Kinetic growth modes of Si in the submonolayer regime on vicinal Ge(100) surfaces miscut by 2.7° and 5.4° towards the [011] direction were investigated using low energy electron diffraction (LEED) and photoelectron spectroscopy (XPS, UPS). At a Si coverage around 0.5 ML and temperatures between 470 and 600 K Si nanostripes separated by Ge nanostripes are formed due to preferential nucleation of Si adatoms on the (1 × 2)-reconstructed Ge(100) domains. At room temperature both Ge(100) domains are covered by pseudomorphic Si islands. The stability of the Ge–Si stripe structure is limited to 600 K above which alloy formation was found by photoelectron spectroscopy.

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1. Introduction

The combination of Ge with Si in heterostructures both as isolated strained layers or as $\text{Ge}_x\text{Si}_{1-x}$ alloys has been found to be effective for tailoring electronic properties, e.g. to increase mobilities, in electronic devices [1,2]. For further miniaturization there is an increasing demand for control of structure and composition on the atomic scale, especially at the interfaces. Studies of vic-

inal surfaces, on the other hand, offer additional possibilities of structuring and modifications of electronic properties by self-organization [3,4]. Furthermore, electron confinement on the scale of only a few nanometers at room temperature needs the combination of thin layers of semiconductors with those of wide band gap insulators. Here defects on surfaces (e.g. point defects or steps) become of dominant importance, because they dramatically influence the adsorption behavior [5].

Stepped surfaces provide a symmetry reduction compared to flat, highly symmetric closely packed surfaces. Due to the higher coordination of adatoms at step edges their binding energy is higher

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than on terraces. Thus regularly stepped surfaces provide, in contrast to other defect structures, good templates for the generation of chains along the steps, e.g. for nanowires. Stepped structures can be quite easily characterized and controlled in an experiment and also their equilibrium structures have been described successfully using atomistic models as well as elasticity theories (e.g., see [6] and references therein).

Steps are also known to influence diffusion by providing additional barriers due to the Ehrlich–Schwoebel effect. Exploiting this effect in a controlled manner allows the formation of kinetically favorable, but metastable structures. One of the best known examples is the effect of step bunching on clean Si(111) surfaces induced by electromigration [7].

Comparing vicinal surfaces of Si and Ge close to the (100) orientation, the step morphology of both systems is remarkably different, mainly due to significant differences in the step–step interaction energies [8]. This has the consequence, as explicitly shown for Ge surfaces miscut by 2.7° and 5.4° with respect to the (100) plane towards the [011]-direction, that even for large miscut angles vicinal Ge(100) surfaces consist predominantly of steps with single atomic height [8]. As a detailed analysis showed, relaxations of Ge atoms at terrace and step sites are much smaller than those on corresponding vicinal Si surfaces. This results in weaker strain fields, i.e. the interaction between steps are lower on Ge than on Si. As a consequence, the formation of steps with double atomic height should occur for vicinal Ge(100) at miscut angles close to 9° [8]. In this case the terrace length is around 2 unit cells, i.e. usually too short for epitaxial growth. In contrast, the critical angle for double step formation on vicinal Si(100) is around 2.5° [9].

The formation of steps with double atomic height is of importance, since for perfect lattice matching not only the lateral structure has to match with, e.g., an insulating layer to be grown on such a surface, but also the step structure. This is easily seen in the case of an NaCl(100) film on Ge(100), where the step height of fcc NaCl is twice that of Ge, whereas the lateral lattice constants match within 0.5%. If a vicinal Ge surface can be grown that contains exclusively double steps, the

possibility of imposing the step structure of the substrate onto the insulator is feasible, resulting in a regularly stepped insulating NaCl(100) film [11]. NaCl(100) epitaxy with a high step density was performed successfully by pre-adsorption of Si on a vicinal Ge(100) surface.

In this study we demonstrate that the formation of double steps can be induced by Si adsorption on vicinal Ge(100) surfaces by appropriate kinetic growth conditions resulting in a surface with good thermal stability. This results in an alternating sequence of stripes of bare Ge and those covered with 1 monolayer (ML) of Si. However, as will be shown, it happens only in a small parameter window.

2. Experiment

The experiments were carried out under UHV-conditions at a base pressure of 1×10^{-8} Pa. The chamber was equipped with a SPA-LEED instrument to access the surface morphology and with electron spectroscopy techniques (XPS, UPS, and EELS) for determining the chemical state and the electronic properties of the surface.

The vicinal Ge(100) surfaces were oriented using a Laue camera, and were polished afterwards with diamond paste (smallest grain size $0.25 \mu\text{m}$) followed by a final cleaning in propanol, acetone and deionized water. Before transferring the crystal into the UHV-chamber, the Ge surface was exposed to ultraviolet light in an oxygen atmosphere to decrease the contamination as well as to grow a protective oxide layer on the crystal surface [12]. The oxide was removed afterwards in situ by thermal evaporation keeping the sample at 670 K for several hours. As pointed out earlier [8], the ozone treatment significantly shortens the sputtering time (sputtering with 800 eV Ar^+ -ions, $1.5 \mu\text{A}$ crystal current at 300 K, followed by annealing to 900 K). The temperature of the surface was controlled by a Ni/NiCr-thermocouple, which was spotwelded to a piece of Ta foil and directly clamped to the crystal. This guaranteed reproducibility below 1 K, with an uncertainty of absolute temperature reading of less than ± 20 K.

Silicon was evaporated from a vitreous carbon crucible, heated by electron bombardment with a

tungsten filament, located around the front end of the crucible. Typical evaporation rates were 0.03 ML/s at a pressure of 5×10^{-8} Pa. To obtain these conditions, extended outgassing for several days was necessary. The coverage was calibrated using XPS by measuring the attenuation of the Ge2p_{3/2} emission. Although this peak is the most intense, the error bars of the absolute amounts are around 0.1 ML since the atomic sensitivity factors are not known accurately.

3. Results and discussion

The aim of the present study is to explore possibilities for the formation of a single domain structure on a vicinal Ge(100) surface, i.e. to create a surface with only D_B steps. This turns out not to be possible by simple miscut. Therefore, we tried to make use of the known anisotropic diffusion of adatoms on (2×1) reconstructed semiconductor surfaces by depositing Si onto vicinal Ge surfaces. As expected, this mechanism can only be effective over a small range of Si concentrations and a specific temperature range. This is seen by comparing results at various Si concentrations and temperatures. We present the behavior of adsorbed Si under various growth conditions to underline the small range of parameters for a successful Si-induced D_B step formation, but first show our results concerning the kinetic step bunching effect on Ge(100)-[011] 2.7° and Ge(100)-[011] 5.4° surfaces at close to half-monolayer Si coverage.

3.1. Si-induced double step formation

Examples of the clean vicinal Ge surfaces are shown on the left of Fig. 1 for the Ge(100)-[011] 2.7° and Ge(100)-[011] 5.4° surfaces. The spot splitting of the integer order spots stems from the vicinity of the (100) surface and corresponds to a miscut along the [011]-direction [8]. The clean Ge(100)-[011] 2.7° and the Ge(100)-[011] 5.4° surfaces (see Fig. 1a and c) at room temperature show two rotational domains of the (2×1) structure with spots broadened by the small size of the terraces. As shown in Ref. [8], both the Ge(100)-

[011] 5.4° and the Ge(100)-[011] 2.7° surface consist basically of an alternating arrangement of (1×2) and (2×1) reconstructed (100)-terraces separated by steps of single atomic height, e.g. the average terrace length for the Ge(100)-[011] 5.4° surface is 15 Å. In contrast to the integer order spots, the half order spots are not split, indicating that there is no correlation between domains of the same orientation. As demonstrated in Ref. [8], even for a vicinal Ge containing only steps of single atomic height, the observed spot splitting always corresponds to twice the average width of a single terrace for two reasons: First, the (2×1) reconstructed domains are larger on average, i.e. destructive interference is never complete. Second, at non-normal incidence (as used here) scattering from the two domains is not equivalent even for integer spots. Thus the maximum spot splitting, e.g. for the Ge(100)-[011] 5.4° surface is 13% Brillouin zone (BZ) not 26% as expected for a surface with steps of single atomic height.

If Si is evaporated onto these surfaces at 0.03 ML/s at elevated substrate temperatures around 470 K with a final concentration between 0.5 ML and 1 ML, we obtain the results shown in Fig. 1b and d for the Ge(100)-[011] 2.7° and Ge(100)-[011] 5.4° surfaces.

The domain with half-order spots along the step edge direction ([011]-direction) has completely vanished, but the half-order spots corresponding to the (2×1) reconstruction domain remain. This can be seen even better in Fig. 2 from the line scans along the [011]- and the $[0\bar{1}1]$ -direction of the Ge(100)-[011] 5.4° surface indicated by arrows in Fig. 1c and d before and after adsorption of 0.5 ML Si.

The half-order spots of the remaining (2×1) domain on the Si/Ge(100)-[011] 5.4° surface are now partially split indicating significant correlation of the reconstruction on different terraces. It is hardly conceivable that such correlations would be effective with an intermediate terrace of different structure in between. We take this finding as an indication that equivalent terraces are formed by Si adsorption with a preferred (even or odd) terrace length. Thus domains on adjacent terraces have the same rotational orientation with the doubled period normal to the steps. This corresponds

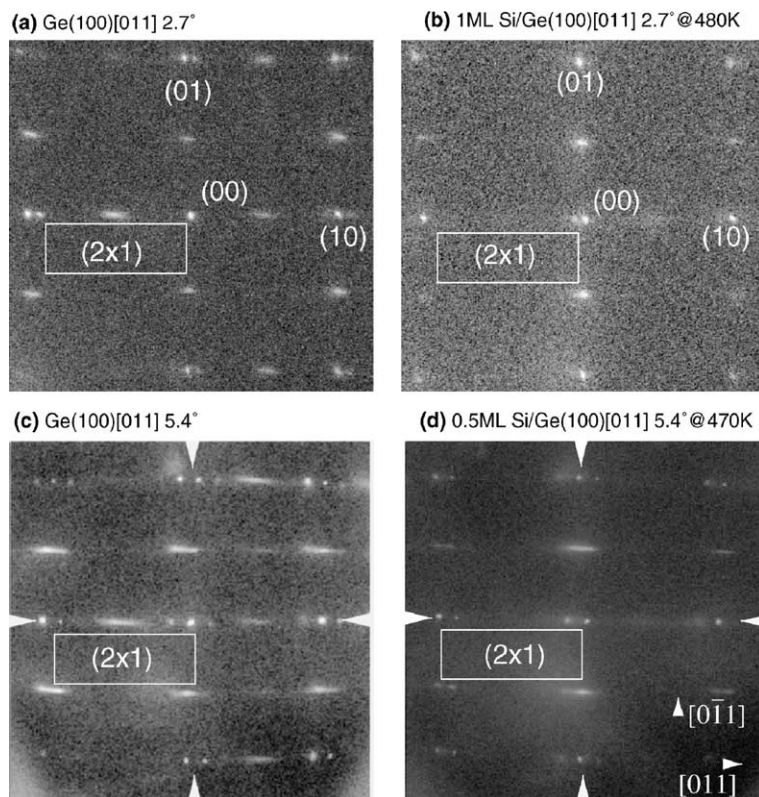


Fig. 1. Formation of single domain structures on Ge(100)-[011] 2.7° (top) and on Ge(100)-[011] 5.4° (bottom) surfaces after adsorption of silicon (right) at temperatures around 470 K. Line scans along the directions indicated by the arrows are shown in Fig. 2.

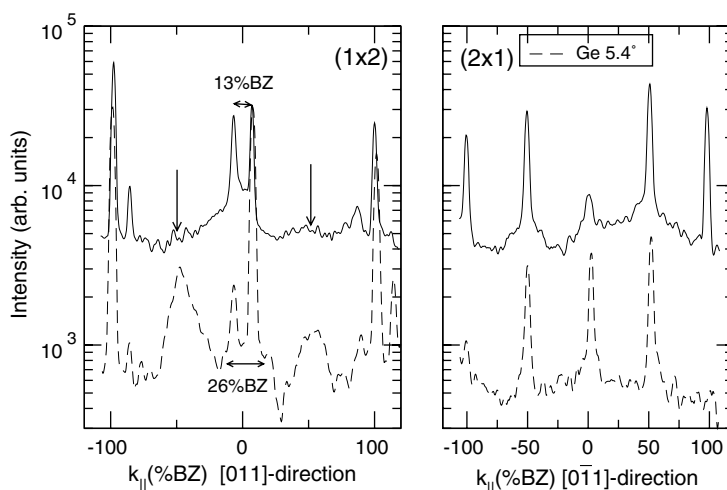


Fig. 2. Line scans perpendicular (left) and parallel (right) to the step edges before (dashed lines) and after adsorption (solid lines) of 0.5 ML Si at 470 K on a Ge(100)-[011] 5.4° surface on the same intensity scale recorded at 300 K.

for the Ge(100)-[011] 5.4° surface to a terrace length of 30 \AA separated by diatomic steps (2.8 \AA).

The disappearance of the other rotational domain must be caused by selective adsorption of the half monolayer of Si on this domain. The domain disappears either because it is transformed into the surviving domain or the reconstruction is eliminated on this part of the surface due to the stress induced by the adsorption of Si. The latter mechanism seems to be reasonable here, since it was found years ago for the adsorption of Ge on Si(100) [10]. Further experimental evidence for this removal of the reconstruction on the Si covered parts of the surface, as revealed by adsorption experiments done at 300 K, will be given below.

For the selective growth of Si nanostripes on one domain at least two mechanisms are necessary: a strong anisotropy of diffusion and an Ehrlich-Schwoebel barrier. The effect of anisotropic diffusion is well-known and was observed in particular for the homoepitaxial system Si/Si(100) [17] and for Ge/Si(100) [18,19]. Due to the dimerization of these (100) surfaces and the associated geometrical relaxations, the potential barriers between dimer rows are higher than along dimer rows. This results in a much higher diffusion constant for adatoms along the dimer rows, in agreement with our experimental observation.

To keep the Si atoms predominantly on just a single terrace of the original Ge surface, there must be an Ehrlich-Schwoebel barrier (ESB) at the Ge step edges. This is illustrated in the left part of Fig. 3. As a clear indication for the existence of the ESB, as we will show below, the preference

for the population of the (1×2) domain by Si at substrate temperatures around 300 K disappears. From these findings the thermal activation energy to overcome the barrier can be estimated to be around 15 meV, i.e. a factor of two lower than for Si(100) surfaces [16]. An additional anisotropy of the ESB, as indicated in Fig. 3 when crossing a step with different orientations of the reconstruction, may even enhance the effectiveness of the ESB. In addition, the stronger Si-Si bonds compared to Ge-Si and Ge-Ge bonds favor Si island formation and stabilize the Si islands once they are formed. The resulting structure is shown schematically on the right of Fig. 3. Even under most favorable conditions, the filling of a single domain with Si atoms can never be perfect from entropy considerations. The disorder thus introduced by point defects (single Si atoms, vacancies) is directly visible in LEED from the increased background (see Fig. 2).

Although perfect formation of a double-step structure must depend on the exact amount of material deposited and on the temperature, complete extinction of the minority domain can be observed if the coverage is larger than 0.5 ML. This is illustrated by Fig. 1b for the Ge(100)-[011] 2.7° surface with 1 ML Si at the same temperature. Although the background intensity in LEED has increased significantly, indicating a less perfect surface, the LEED spots of only one (2×1) domain remain. This finding indicates a preference for the formation of Si islands that are higher than one Si layer under the growth conditions used, a second layer of Si grows on top of the first layer, but still no reconstruction in the strained layers is observed.

Even though the model of anisotropic diffusion seems to be reasonable in our case, other models have been discussed in the literature: e.g., Mo et al. [20] showed in their STM measurements, supported by Monte Carlo calculations, that the formation of anisotropic Si islands adsorbed on Si(100) can be explained simply by lateral anisotropic accommodation coefficients, i.e. the velocity of the two different growth fronts differ by one order of magnitude on Si(100) so that one domain can catch-up to the other one, resulting in bilayer steps. However, the homoepitaxial growth model with anisotropic diffusion fits the experimental data

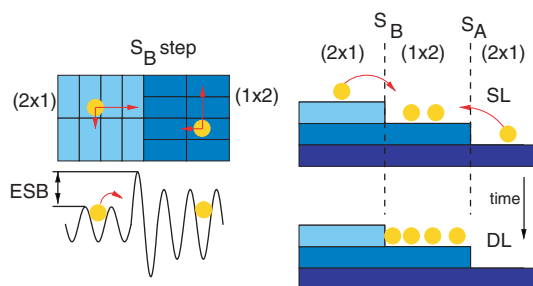


Fig. 3. Schematic of the anisotropic diffusion process of Si atoms on Ge(100) terraces at $T = 470\text{ K}$ resulting in predominant population of only the (1×2) domain by the Si atoms.

much better, as demonstrated in a later publication of the same group [21]. The diffusion of an Si adatom was assumed to be a thousand times faster along the dimer rows than perpendicular to them.

3.2. Si growth at room temperature

The pseudomorphic growth of Si on one domain is strongly dependent on coverage and on surface temperature due to the temperature dependence of diffusion and the ESB. This is seen directly by repeating similar experiments at room temperature, where the mode of selective adsorption on only one domain is no longer present. As an illustration, we show in Fig. 4 LEED patterns of a Ge(100)-[011] 5.4° surface (Fig. 4(a)) and this surface with silicon coverages of 0.4 ML (b) and 2 ML (c) adsorbed at room temperature.

As can be seen in Fig. 4, the adsorption of 0.4 ML Si leads to attenuation of the half-order spots. At 2 ML Si at 300 K the half-order spots vanish completely and the background increases strongly. More details of this behavior are shown in Fig. 5 for the Ge(100)-[011] 2.7° surface. In this experiment, we gradually increased the Si coverage up to 0.3 ML. The deposition temperature was again 300 K. Similar to the Ge(100)-[011] 5.4° surface the half-order intensity decreases monotonically and simultaneously for *both* domains, in contrast to the adsorption of Si at 470 K. (cf. with Fig. 2), whereas the background increases. The increase of the background, combined with a constant halfwidth of the spots, indicates a random distribution of Si atoms on the surface [13]. Obviously, the mechanism for step bunching induced by Si adsorption at elevated temperatures, has become ineffective. Although the damping of the half-order spots perpendicular to the step edges is stronger compared to the parallel direction (cf. with Fig. 5), the probability to overcome the ESB of both S_A and S_B steps at room temperature is much smaller than at 470 K. However, the experiments at 300 K show clearly, that the strained Si film itself is not dimerized.

Another important question is of course whether dimerization at the interface between both the Ge(100)-[011] 5.4° and the Ge(100)-[011] 2.7° surface and the Si film is destroyed after the

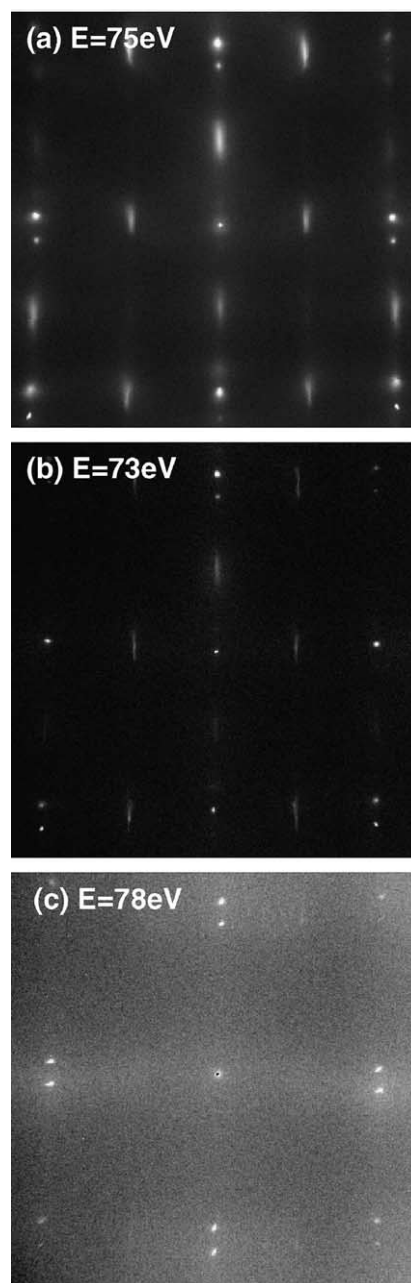


Fig. 4. LEED pattern of the first BZ of a Ge(100)-[011] 5.4° surface after different treatments: (a) clean surface, (b) deposition of 0.4 ML Si at 300 K, (c) 2 ML Si at 300 K. The intensity scale is chosen to be the same for graphs (b) and (c).

adsorption. The fact that for coverages far below 0.5 ML a significant reduction of the intensity at

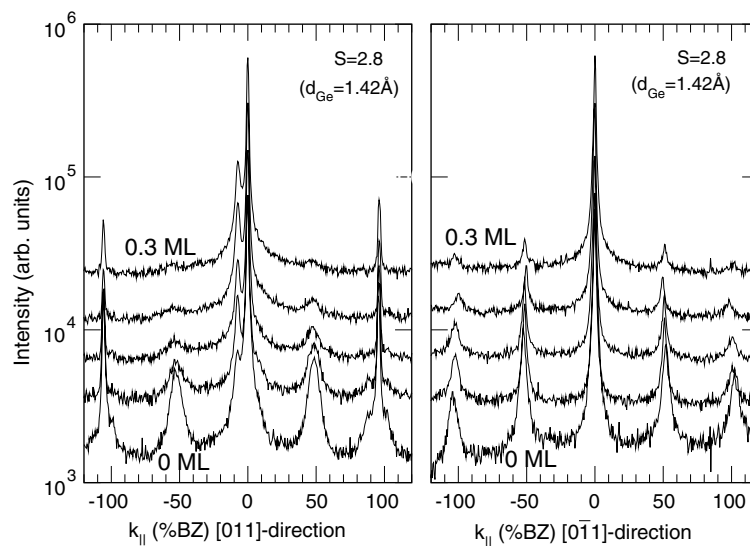


Fig. 5. Line scans perpendicular (left) and parallel (right) to the step edges of a Ge(100)-[011] 2.7° surface for Si coverages between zero and 0.3 ML increased in equidistant steps of coverage. $T = 300$ K.

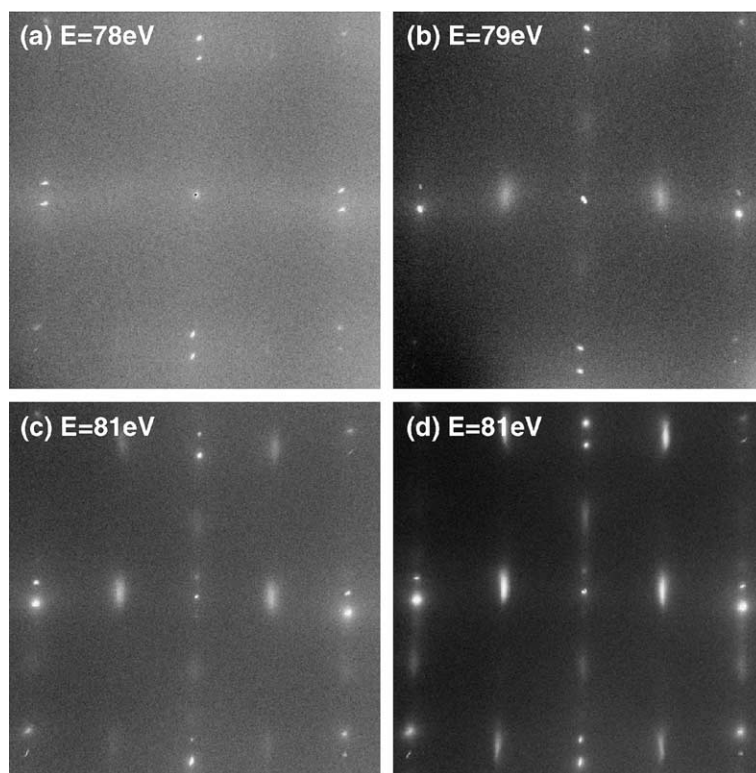


Fig. 6. LEED pattern of the first BZ of a Ge(100)-[011] 5.4° surface after different treatments: (a) 2 ML Si adsorbed at 300 K on Ge(100)-[011] 5.4° (b) after annealing of the film to 500 K, (c) to 700 K, (d) to 900 K. The intensity range is chosen to be the same for all four graphs.

50% BZ is seen indicates pseudomorphic Si islands on Ge that remove the reconstruction. This is supported by UPS measurements of a clean Ge(100)-[011] 2.7° surface and this surface covered with 1 ML Si. The surface state approximately 0.6 eV below the valence band maximum of a Ge(100) surface characteristic of the (2×1) reconstruction [14,15] is significantly reduced in intensity after the deposition of Si. The limited resolution of our instrument, however, did not allow the surface resonance to be resolved.

3.3. Surface alloy formation

Although there are apparently no structural changes visible in LEED when the Si layers are annealed to temperatures above 600 K (see Fig. 6), the thermal stability of the adsorbed Si layers turns out to be limited to approximately 600 K as revealed by XPS. After adsorption at room temperature and annealing, the measurements were carried out at room temperature to avoid any changes of the background by Debye–Waller contributions. Qualitatively, annealing to higher and higher temperatures reduced the background intensity in LEED, and both half-order spots for each reconstruction domain appear again, so that the final state (d) in Fig. 6 looks quite similar to the clean Ge surface (cf. with picture c in Fig. 1). This impression, however, is misleading, as the XPS analysis shows (see Fig. 7). This sequence of experiments also demonstrates that the formation of Si nanostripes by post-annealing is not possible.

The XPS data shown in Fig. 7 was recorded from a 1 ML Si film was deposited at 300 K and the temperature was subsequently increased to 900 K. The integrated intensities of the most intense photopeaks of the substrate and of the adsorbate, respectively, namely the $\text{Ge}2p_{3/2}$ and the $\text{Si}2p$ emissions, are plotted in Fig. 7. Please note that, because of their very different binding energies, the mean free paths of the photoelectrons differ by approximately one order of magnitude. Interestingly, the Si intensity remains more or less constant within the whole temperature range, whereas the $\text{Ge}2p_{3/2}$ intensity increases significantly above a critical temperature, which is

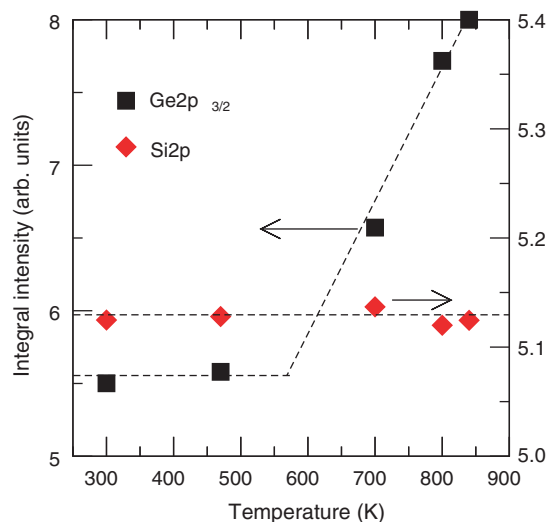


Fig. 7. Integral intensity of the $\text{Ge}2p_{3/2}$ and $\text{Si}2p$ emissions determined by XPS as a function of temperature of a 1 ML Si film evaporated on Ge at 300 K. The intensity of the $\text{Si}2p$ emission is shifted linearly for better visibility.

approximately 600 K as determined by simple extrapolation. This is direct evidence that Ge and Si atoms were redistributed by annealing, although the LEED pattern looks rather the same.

Since Si cannot be desorbed from a Ge surface by annealing to these temperatures, two possibilities can explain our experimental finding: Either the Si atoms become mobile and Si islands several layers high are generated to reduce the stress within the film, or Si forms an alloy with the topmost Ge layers. Both mechanisms would lead to an increase in the Ge XPS intensity relative to the Si intensity. Although both models are able to reproduce the observed changes in intensity the alloying model seems more plausible: The model with pure strained Si islands would require to uncover more than 80% of the surface to form islands that are more than 5 layers high. The build-up of stress in these islands can be reduced considerably by the formation of mixed islands or layers. The formation of Ge–Si alloys under comparable conditions is well known [22]. From the constancy of the Si XPS intensity we conclude that the alloy formation must be limited to roughly three monolayers. While we are not able to determine the exact distribution of the Si concentration, we note that

the reduction of stress in these alloys allows the (2×1) reconstruction to reappear.

4. Conclusion

In conclusion, we observed three different regimes for the growth of Si on vicinal Ge(100) surfaces in the low coverage regime up to 2 ML. At 300 K a pseudomorphic and essentially isotropic growth was observed. Above a critical temperature of 600 K alloying sets in, as seen by XPS.

The most interesting growth mode was observed at intermediate temperatures around 470 K, because a selective growth of Si nanostripes on the (1×2) terraces was found. Using this method we were able to generate a vicinal Ge surfaces with steps of double atomic height. Due to their thermal stability they may be useful as single domain surfaces similar to corresponding Si surfaces, but with different properties.

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