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Layer-by-layer growth of germanium on Si(100): strain-induced morphology and the influence of surfactants

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Germanium grows on pure Si(100)-(2×1) in the Stranski–Krastanov mode. Layer-by-layer growth is found for coverages below 3 ML before the onset of 3D islanding. In this regime the morphology of the Ge layer is strongly influenced by the misfit of 4.2% between layer and substrate. Around 1 ML aligned missing dimer defects are created which form a semiperiodic (2×12) arrangement. With increasing coverage this periodicity is gradually compressed and reaches a (2×8) reconstruction around 2.3 ML. This behaviour is discussed in terms of partial relaxation of the local strain. When further Ge layers grow on this (2×N) arrangement, only part of the missing-dimer defects of the lower layer are buried and a network of trenches partly reaching down to the substrate remains. Layer-by-layer growth up to higher coverage can be obtained using As as a "surfactant" during growth. Under these conditions no (2×8)-like arrangement is found. Up to 12 ML Ge coverage the layer grows free of defects forming extremely anisotropic Ge islands. At higher coverage a network of trenches arises which decorate an array of V-shaped defects previously found with TEM. The arrangement and the start of the overgrowth of these defects is studied.

1. Introduction

The strained-layer growth of germanium on Si(100) is of fundamental interest as a model system for misfit-related growth (4.2% misfit). The growth system is known to be of the Stranski–Krastanov (SK) type which means in this case layer-by-layer growth up to 3 ML (1 ML = 6.78×10^{14} atoms/cm^2) followed by the formation of 3D islands. It has been shown that an intermediate phase exists where germanium forms regular faceted "hut-shaped" islands [1] before at higher coverage relaxed 3D islands appear. The purpose of this investigation was to study the layer-by-layer growth regime (1–3 ML) which is also interesting for device applications because of the special electronic properties of the strained Ge layers, i.e. in Si–Ge multilayers [2]. On the other hand, germanium could act as a template for GaAs growth on Si(100) as an intermediate layer. Also for these practical reasons it is important to know the exact morphology of the thin Ge layers grown on Si substrates.

A recently developed method [3] to force layer-by-layer growth of germanium on Si(100) up to higher coverages is to use an As layer floating on the surface of the growing species as "surfactant". Surfactants lower the surface free energy of both the substrate and the adlayer and can therefore change the growth mode drastically. Our goal was to obtain exact information about the surface morphology to learn more about the way the surfactants work. V-shaped defects [4] in the Ge layer have been identified by TEM which provide continuous relaxation of the strain with increasing layer thickness. The influence of these bulk defects on the surface morphology is also shown in this study.

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2. Experiment

50 mΩ Si(001) samples with a random miscut of about 0.07° were used as substrates. After degassing, the surfaces were cleaned by thermal desorption of the native oxide at 1050°C followed by several short temperature flashes to 1250°C. Germanium was deposited in situ onto these samples from a boron nitride crucible. The evaporation was monitored by a quartz microbalance. The Ge deposition was done with the substrate at the indicated temperature; STM micrographs were taken after the sample had cooled down to RT. With Auger spectroscopy it was checked that for the deposition temperatures used in our studies no interdiffusion of Si and Ge takes place. Therefore, all surface atoms seen in the STM images are Ge or As. All images shown in this paper were obtained with a negative bias at the sample (tunneling from filled states of the surface). The LEED measurements were performed in a separate UHV chamber under identical conditions.

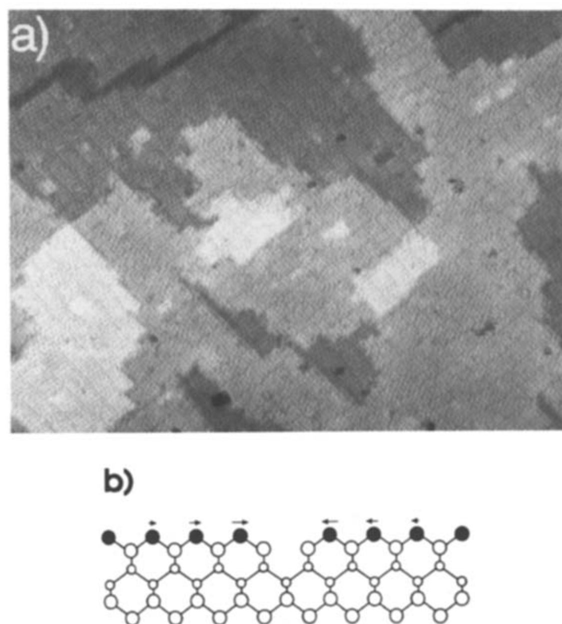

Fig. 1. (a) 1.4 ML Ge deposited at 450°C substrate temperature. The image shows an area of 1000 Å × 730 Å. (b) Model for the observed superperiodicity (cut perpendicular to the surface).

3. Results and discussion

The submonolayer growth regime has been intensively studied [5,6]. Therefore, we just want to summarize our results for this regime which are essentially identical to the literature. Ge islands formed in the submonolayer range are asymmetrically elongated perpendicular to the direction of the dimer rows of the substrate but the asymmetry is less pronounced as in the case of the growth of silicon on Si(100). This is an indication that also in the case of Ge growth the two possible step edges of the substrate are nonequivalent with respect to their ability to collect diffusing adatoms. The dimer rows of the epitaxial Ge islands nearly exclusively consist of buckled dimers, in contrast to the growth of Si on Si(100) [7]. The buckling in adjacent dimer rows is with equal propability in and out of phase, leading to local arrangements with (2×2) and $c(2 \times 4)$ symmetry. The diffusion behaviour of germanium in the submonolayer range has been proven to be very similar to the diffusion of Si on Si(100), i.e. a strongly enhanced diffusion along the dimer rows of the substrate [5].

In the submonolayer range, on larger islands, missing-dimer defects are visible which are aligned in the direction perpendicular to the dimer rows. Upon closing the first monolayer the number of these defects increases and above 1 ML the surface looks like shown in fig. 1a. A nearly perfectly ordered network of aligned missing-dimer defects is visible with a defect distance of ~ 10 dimers adding a second periodicity perpendicular to the dimer rows. Therefore a (2×10) reconstruction results. (Because the distance of the defects is not constant with changing Ge coverage (see below) the reconstruction is referred to as "(2×8)" in this paper.) Images with higher resolution show that exactly one dimer is missing in contrast to the case of the Si(100)-(2×8)/Ni, where a similar superperiodicity but with a more complex missing-dimer structure was observed [8]. To exclude any Ni contamination, we took Auger spectra which show no traces of any metal contamination concomitant with the Ge

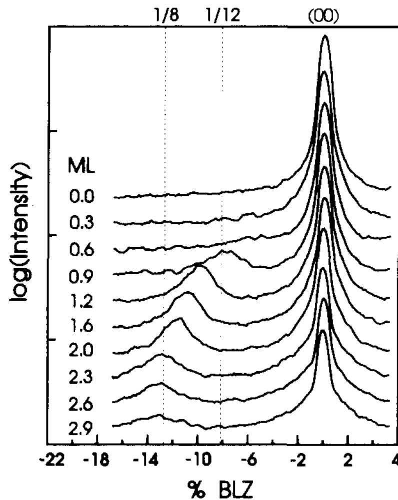

Fig. 2. Sequence of LEED-spot profiles for the Ge coverages as indicated. The spot left of the (00) spot is caused by the "$(2\times N)$" periodicity. (100% BLZ = distance from (00) to (10) spot.)

deposition (sensitivity 1/500). As in the case of the Si(100)-(2×8)/Ni, the $(2\times N)$ missing-dimer structure can be explained as being caused by stress in the epitaxial layer. In the present case the stress is caused by the misfit between substrate and adlayer. LEED shows that up to 3 ML the Ge layer adopts laterally the Si lattice constant. In fig. 1b a possible model is shown. The gap in the layer may allow the Ge layer to expand and therefore to reduce part of its strain, at least in one direction.

In order to determine how the missing-dimer structure develops with increasing coverage, we performed a high-resolution LEED measurement [9], where the diffraction intensity between the (00) and (10) spot was measured during the Ge deposition. Fig. 2 shows a sequence of these spot profiles with increasing coverage. Around 0.8 ML a spot left of the (00) appears in a position roughly corresponding to a (2×12) reconstruction. With increasing coverage it continuously shifts towards a shorter periodicity ending up in a (2×8) position around 2.3 ML. The maximum intensity of the superstructure peak is around 1.4 ML, which becomes understandable from the growth behaviour at higher coverage. The continuous shift in periodicity of the missing-dimer defects shows that the structure is not strictly periodic but consists of a mixture of distances whose average value gives rise to the spot in electron diffraction. If we assume the (2×8) structure as caused by the misfit-induced strain, the higher density of missing-dimer defects with increasing coverage could be the reaction of the surface to compensate for the increasing strain in the Ge layer by introducing more missing-dimer defects. A similar behaviour has also been found for the Si(100)-(2×8)/Ni surface with increasing Ni contamination [10].

It is obvious that the growth mode with the missing-dimer defects can not easily be continued above 1 ML Ge coverage. The missing-dimer defects in the first layer have either to be filled, if a next Ge layer is grown or there have to be trenches in the second layer in the locations of the missing-dimer rows of the first layer. Of course, the first possibility would increase the strain in the Ge layer.

The surface actually realizes a mixture of both possibilities mentioned above (fig. 3). Fig. 3a shows three terraces separated by monatomic steps of a 3 ML thick Ge layer. The surface consists still exclusively of buckled dimers. On the terrace in the middle of the image the dimer rows run from the upper right to the lower left, the missing-dimer defect lines perpendicular to this direction (better visible in the higher magnification of fig. 3b). In addition to these structures a quite irregular trench structure parallel to the dimer rows of the outermost layer is visible. Fourier-transforming this structure yields an average periodicity of ~ 12. The trenches reach down to the first layer. In a few locations even deeper trenches can be seen, again rotated by 90° which reach down to the substrate. The trenches in the outermost layer also lead to smaller domains in the (2×8) reconstruction which is responsible for the decrease in intensity of the associated LEED spot in fig. 2.

From these observations the following scenario of the growth behaviour can be deduced: The first Ge monolayer shows missing-dimer defects which allow the adlayer to reduce part of its strain. For the second layer there is a competition between the minimisation of surface energy by

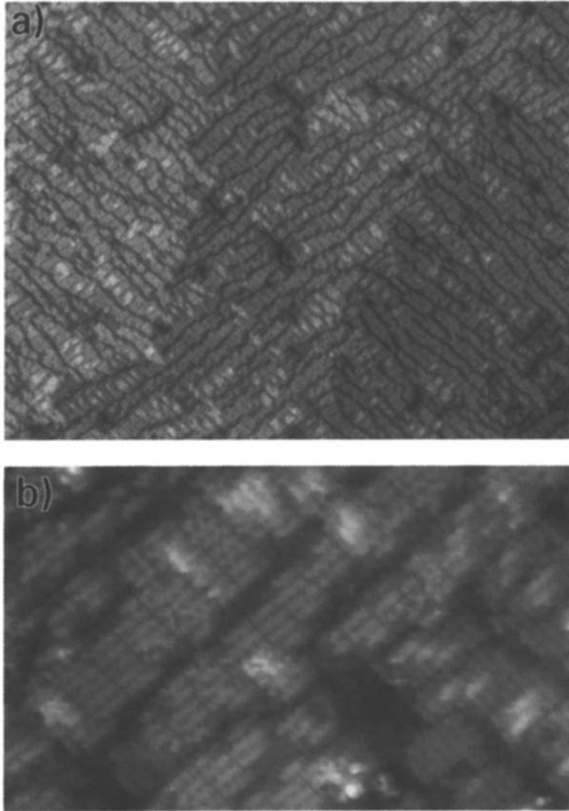

Fig. 3. (a) 3 ML Ge deposited at 450°C. The overview image (2000 Å × 1600 Å) shows the trench structure perpendicular to the dimer defects in the outermost layer. (b) Higher-resolved image (300 Å × 200 Å) showing details of the (2 × 8) reconstruction and the trench structure.

forming a closed layer and the reduction of strain by leaving gaps in which the layer can laterally extend. On average every second missing-dimer defect of the first layer is filled. With the third Ge layer most of the gaps in the first layer are filled and the same relation is now valid for the second and the third layer. The substrate is never completely covered by the adlayer which forms a quit open structure. The filling of the defects of lower levels increases the strain in the layer in that way, that for a Ge coverage of more than 3 ML it is more favourable to form "hut clusters" which are completely relaxed.

For the low deposition rates used in our study, layer-by-layer growth up to higher coverage can only be achieved by using a third element as surface-active species. The surfactant-mediated germanium growth was performed analogous to the procedure described in ref. [3]. Prior to Ge deposition the surface was saturated by an As monolayer at 500°C. The Ge growth took place at 490°C substrate temperature. Because the As layer is partly desorbing at these temperatures an As overpressure was supplied during growth. These experimental conditions keep the surface capped by arsenic before and after Ge deposition.

Fig. 4a shows the substrate surface after the As-capping before Ge deposition. The surface has substantially roughened. Islands of dimer rows have been formed. As known from the literature [11–13], arsenic forms on the Si(100) surface a stable (2 × 1) reconstruction. All dimers are symmetric. The appearance (only symmetric dimers, spectroscopic behaviour) of the surface is the same on the islands and in between, therefore it is assumed that 1 ML of As covers the surface. The Si surface underneath the As layer has roughened. STM images of As adsorption on stepped Si(100) surfaces have shown [13] that at higher temperature As replaces the outermost Si layer. In this process the excess silicon seems to form islands, if the step density is too low to reach a step edge.

In fig. 4b 2 ML Ge have been deposited. At this coverage and also at higher coverage only symmetric dimers are present at the surface indicating that always a monolayer of arsenic is present. Extremely small, anisotropic islands have been formed, which in most case consist of single dimer strings. Without the presence of As more symmetric islands a few hundred Å wide would form at this substrate temperature. Arsenic seems to change the energetics of step formation. The difference for the two types of steps (parallel or perpendicular to the dimer rows), which is also present for pure Ge deposition is strongly enhanced. The small size of the Ge islands at the relatively high deposition temperature shows that in the presence of As the diffusion of Ge adatoms is decreased. In this low-coverage regime, long-range diffusion may also be hindered by the rough substrate surface (see fig. 4a). At these coverages

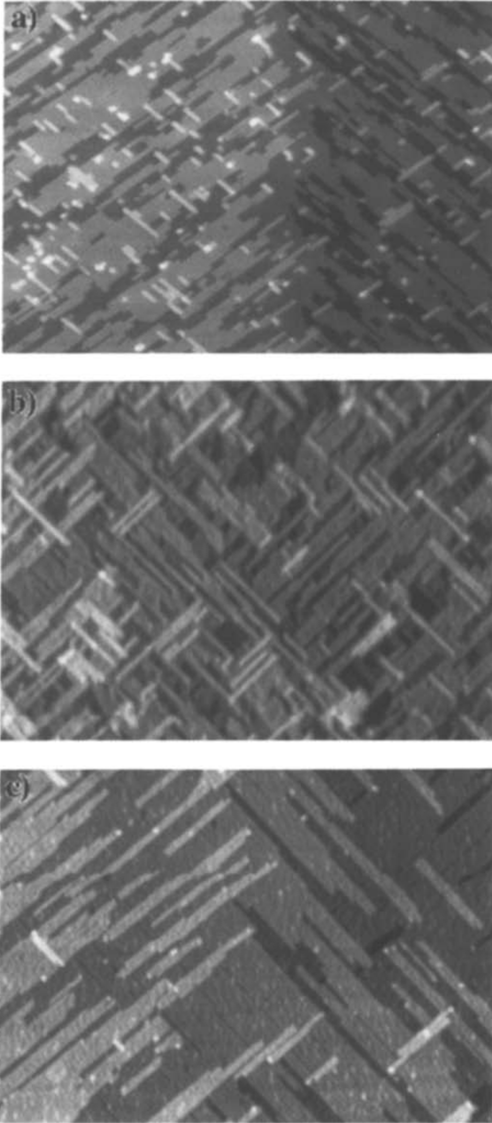

Fig. 4. (a) Si(100)-(2×1)/As surface; As-saturated at 500°C. (All three parts of the image show roughly the same area: 850 Å×580 Å; the influence of steps on the substrate surface is still visible.) (b) 2 ML Ge deposited at 490°C under As overpressure. (c) 12 ML Ge deposited at 490°C under As overpressure; no indication of any defect is visible.

the hindering of diffusion seems to be one contribution to the way the surfactants work.

In fig. 4c the Ge coverage is increased to 12 ML, considerably higher than the critical thickness for layer-by-layer growth without the influence of arsenic. No indication of any 3D island or hut clusters is visible; the surfactant has inhibited the formation of islands. On each terrace the surface mainly consists of only two levels. The Ge islands have grown bigger, but the strong asymmetry is still visible. Surprisingly, also no indication of any stress-compensating defects is found in this coverage range (neither in TEM data [4,14]). Arsenic is known to produce compressive strain on Si and Ge surfaces, which may have an influence but further data are needed to clarify this point.

If the Ge coverage is increased to 24 ML, the morphology of the surface changes completely (see fig. 5). TEM [4,14] shows for this range strain relief by V-shaped defects in the bulk of the Ge layer. This defect consists of two $\Sigma 9$ grain boundaries in $[1\bar{1}2]$ and $[1\bar{1}\bar{2}]$ direction. Several {111} planes are enclosed which provide strain relief by their smaller layer distance (3.14 Å compared to

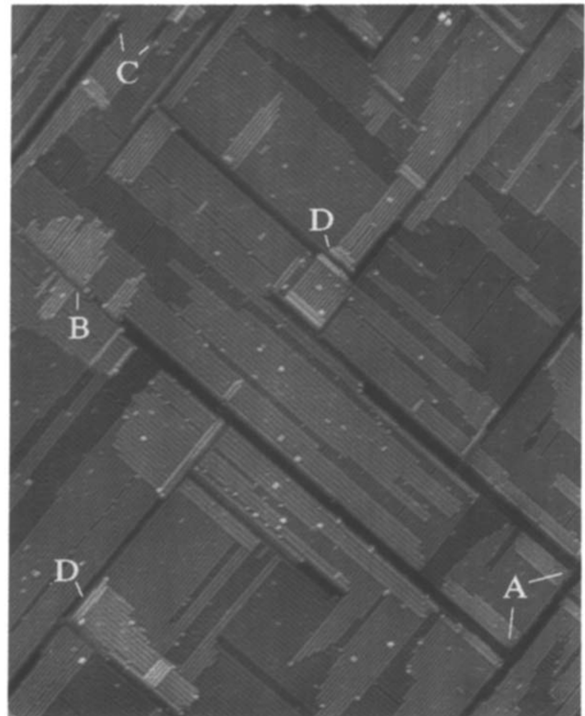

Fig. 5. 24 ML Ge grown at 490°C with As as surfactant. A network of trenches decorates the V-shaped defects. A: intersection of trenches; B: overgrown trench as preferred nucleation site; C: two independently nucleated trenches not passing each other; D: pile-up of germanium at trench boundaries.

3.84 Å). Fig. 5 shows a network of trenches parallel to [01$\bar{1}$] and [011]. These trenches are ~ 30 Å wide and at least 4–5 layers deep. (They may be deeper but the tip did not fit in.) The average distance is 200–300 Å. This distance is identical to the distance in the network of the V-shaped defects as determined from plan-view TEM [4]. The trenches seem to decorate these defects. In between the trenches the surface is still flat and consists of mainly two levels. The average island size is again larger as in the 12 ML case. Islands which have grown far away from a trench display the same asymmetric aspect ratio but most islands are truncated by a trench. The existence of trenches on top of the bulk defects means that in these locations the nucleation of germanium is unfavourable. Fig. 5 shows that the trenches and therefore the V-shaped defects can intersect (location marked A), in contrast to TEM results. Indeed, most trenches are on both sides connected with another trench; there are only a few exceptions. The location marked C in fig. 5 shows two trenches terminating at a distance of 50 Å from each other. These trenches have nucleated independently and are terminated when the stress fields associated with the defects penetrate each other. We never found trenches running parallel in a shorter distance than 60 Å which gives an estimate for the range of influence of an individual defect.

TEM images [14] for higher Ge coverage show that V-shaped defects can be overgrown. In fig. 5 such a location is marked as B. The overgrown area is non-perfect and is therefore a preferred site for nucleation of islands. In general, nucleation of islands is enhanced in the direct neighbourhood of a trench. In fig. 5 two examples are marked as D. One can imagine that these locations are precursors to the beginning overgrowth process.

4. Conclusion

For the layer-by-layer growth without a surfactant STM images show the formation of a relatively open structure consisting of a semiperiodic array of missing-dimer defects. These defects and possibly also the buckling of the dimers in the topmost Ge layer provide partial relaxation of the misfit-induced strain. For the surfactant-mediated Ge growth a strongly reduced diffusion has been found for coverages ≤ 12 ML. The influence of the V-shaped defects on the surface morphology has been imaged and a low probability to overgrow these defects was found.

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