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Smooth growth fronts in Si/Ge heteroepitaxy by kinetic growth manipulation

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A promising route for growing atomically flat Si on Ge(100) is described. The key to this achievement is the control of growth kinetics on an atomic level. We have identified the cause for the development of rough growth fronts: the descent of atoms across steps, a prerequisite for prolonged layer-by-layer growth, is strongly suppressed at double steps. The developedprocedure for smooth growth avoids the formation of these double steps. The approach can be applied at low temperature ($<$550 K) and thus inherently avoids ill chemical definition of the interface due to intermixing. It is expected to be generally applicable for epitaxy of pure Si and Ge on both Ge(100) and Si(100) substrates. [S0163-1829(98)03148-8]

The preparation of smooth films with flat interfaces during heteroepitaxy of pure Si or Ge on Ge or Si substrates is a fundamental problem, because, for these material combinations, flat dislocation-free films are energetically unfavorable. Due to the lower surface free energy of Ge, Ge wets Si, but as a consequence of the 4.2% lattice mismatch, the thickness of the wetting film is limited to a few atomic layers.[1] Beyond that thickness, the elastic strain energy of the pseudomorphic Ge film leads to the formation of three-dimensional clusters.[2] In the inverse configuration even more problems are encountered. Si does not wet Ge and substantial segregation of Ge has been observed above 730 K in layered systems.[3] These fundamental difficulties can be overcome to a large extent by growing SiGe compound films for which the lattice mismatch is reduced or by using surfactants which may change the energy balance of the film/substrate system. Flat films of *pure* Ge/Si or Si/Ge, however, on which the present study is focused, may only be obtained in a metastable state, and hence, growth conditions should in principle be chosen such that the equilibration of the film/substrate system during growth is kinetically hindered.

Unfortunately, under these growth conditions which correspond to low substrate temperatures and/or high deposition rates, films may and in most cases will grow rough because of *kinetic* reasons: not only are the film atoms kinetically hindered to arrange into structures of lowest free energy, but they are also hindered to reach the sites they should fill in order to build the desired metastable structure, i.e., the flat film. The successful development of growth recipes in the kinetic regime therefore requires a detailed understanding of the essential atomic processes and their complicated interplay during growth. By identifying the processes that are responsible for rough growth, kinetic pathways may be found that suppress undesirable and enhance desirable processes. The present paper exemplifies this procedure for the growth of flat films of pure Si on Ge(100). Growth of this system at low temperatures by conventional methods does indeed lead to very rough films as can be seen in Fig. 1(A). By studying the growth of Si/Ge(100) in detail, we have been able to identify the origin of the rough growth: downward diffusion over step edges—the condition sine qua non for layerwise growth—is suppressed at double steps which form naturally during growth at constant temperatures because of the anisotropy of the reconstructed substrate and film. Based on this insight we have developed a kinetic growth recipe which avoids the formation of double steps and thus leads to smooth films, as shown in Fig. 1(B).

Growth and characterization of the films by scanning tunneling microscopy (STM) were performed in ultrahigh vacuum (p$<5\times10^{-11}$ mbar). Prior to film growth the Ge

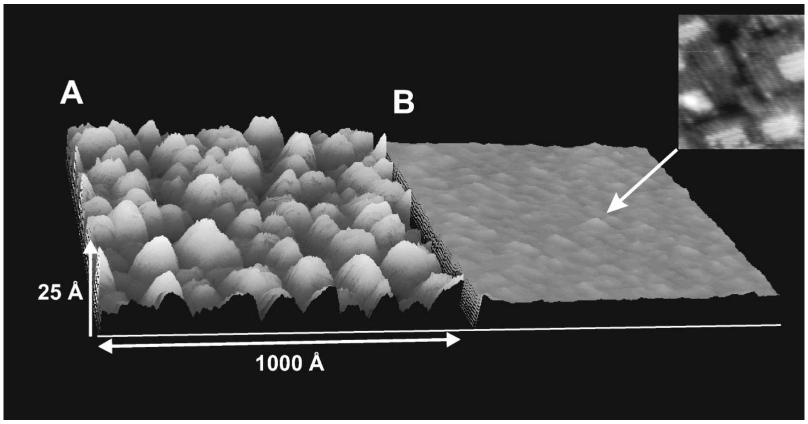

FIG. 1. Morphology of 10-ML-thick Si films on Ge(100). (A) Deposition at constantly 525 K. (B) For each monolayer deposition temperature was varied between 370 and 525 K. The inset displays the local 2×1 reconstruction of the film after growth (160×160 Å^2).

samples were cleaned by cycles of sputtering with Ar$^+$ ions and flashing to 1100 K until no contaminations could be found with STM. This procedure yields nearly defect free Ge(100) surfaces as shown earlier.[4] Si was deposited from a resistively heated wafer with a rate of 0.02 ML/s.[5]

Before we present a detailed study of growth kinetics and develop a recipe to grow flat films at low temperatures, we give evidence for the fact that the rough morphology as shown in Fig. 1(A) is indeed caused by a kinetic mechanism. The very rough film consisting of pyramids or mounds protruding up to ≈15 Å out of the rest of the film results from deposition of 10 (ML) of Si at 525 K. First, this growth temperature is chosen well below ≈800 K, typically used for the strain driven equilibration of Ge films into hut clusters.[2] Second, we observe that the sizes of the mounds vary with deposition temperature but that post annealing of the mounds even up to 600 K does not result in changes in the mound sizes. Hence the formation of these mounds is intimately linked to processes occurring during deposition, i.e., some kinetic mechanism causes the rough growth at these low temperatures. A similar kinetic roughening of the growth front at low temperatures has also been reported for the homoepitaxial systems Si/Si(100) and Ge/Ge(100),[6] where a strain-driven thermodynamic roughening can be excluded right away. Hence it seems that kinetic roughening at low temperatures is common to all these type-IV semiconductor surfaces.

To gain control over the growth mode via enhancement of desirable and suppression of undesirable kinetic processes, we identify in a first step the kinetic process leading to three-dimensional growth. Both the Si and Ge(100) surfaces show a 2×1 reconstruction into rows of dimers along ⟨110⟩ directions. On adjacent terraces, the orientation of the dimer rows is rotated by 90° as a consequence of the diamond structure. During deposition of Si on Ge, the deposited material forms islands that are also 2×1 reconstructed into dimer rows. As many studies of Si and Ge deposition on Si(100) have shown, the reconstruction leads to an anisotropy in both diffusion and sticking.[7–10] As in these studies, we find that diffusion of Si on Ge(100) is fast along the substrate dimer rows and slow across dimer rows,[5] and from an island shape elongated perpendicular to the underlying substrate dimer rows we conclude that the deposited material prefers to stick to the ends of dimer rows of the growing islands instead of to the sides of dimer rows.

It is crucial for layerwise growth that material that lands on top of the growing islands diffuses downwards over the edges of the islands to fill the lower atomic levels before the growth of a new atomic layer starts. We find that downward mass transport, necessary for this smooth growth, is efficient over single steps. Indeed, after deposition of nearly one atomic layer at 475 K, the first layer is almost completed [see Fig. 2(A)]. At a total coverage of 0.92-ML Si, only 0.07-ML Si is found in the second layer, indicating a good mass flow over the step edges of the islands. Moreover, focusing on the second layer islands, one notices that most of these islands [indicated by stars in Fig. 2(A)] are situated at former antiphase boundaries (APB's) of the first layer [also see the inset of Fig. 2(A)]. These APB's are created when two neighboring islands that belong to different translational domain classes of the 2×1 reconstruction coalesce. As in the case of homoepitaxial growth of Si(100),[11] the second-layer islands preferentially nucleate at these APB's, and only a few are the result of homogeneous nucleation. Hence, in the absence of APB's, practically no second-layer islands would have been formed, revealing an efficient downward mass transport. Since diffusion mainly takes place along the dimer rows, one can conclude that the material deposited onto the

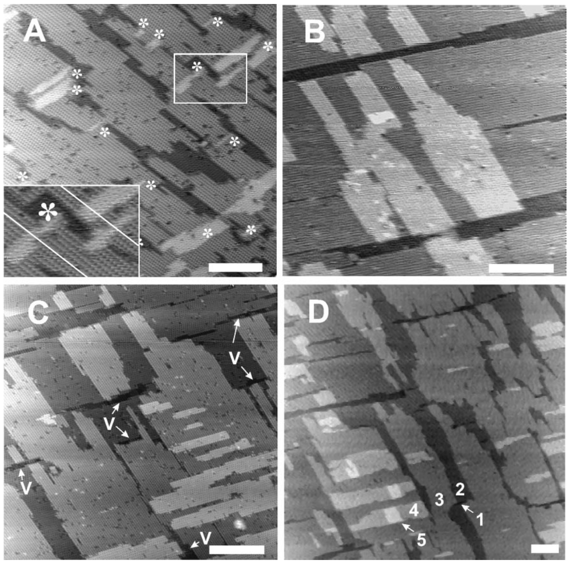

FIG. 2. Filled-state STM images of Si films of 0.92 ML (A), 1.3 ML (B) and 3 ML (C) and (D) grown at 475 K (A) and 525 K (B), (C), and (D). The white bars represent 200 Å. The inset in the lower left of (A) shows an enlarged view of the marked area.

growing islands encounters no substantial additional barrier at the ends of the dimer rows to diffuse down and fill the lower level. In earlier STM studies of the denuded zone around step edges, Mo and Lagally came to this conclusion for Si adatoms on Si(100).[8] The absence of a step edge barrier at the end of dimer rows seems to be a general feature of the (2×1)-reconstructed semiconductor surface.

In contrast to the excellent downward mass transport observed during growth of the first layer, growth of thicker films leads to three-dimensionally rough films. At some point during growth, downward mass transport must be hampered. To find out when and where, we extended the study of the growth scenario to coverages beyond 1 ML. During growth of the first atomic layer, islands elongated perpendicular to the substrate dimer rows expand on the terraces, coalesce, and leave the surface with elongated vacancies, as can be seen in Fig. 2(B). The vacancies are bound by steps preponderantly running along the dimer rows of the islands. During further growth, these vacancies are not filled very efficiently. Direct deposition into the vacancies only slowly fills them up, and only a little material can descend into the vacancies due to the slow diffusion of material across the dimer rows of the first layer toward the long step edges predominantly binding the vacancies. Upon nucleation of the second-layer islands, these islands expand perpendicularly to the dimer rows of the first-layer islands due to the preferred sticking to the end of dimer rows. The expansion of the dimer rows of these second-layer islands eventually stops when they reach a downward step edge of the first-layer islands, and a step, two atomic layers high, is created, as illustrated in Fig. 2(B). However, material is also deposited onto the second-layer islands, which may quickly diffuse along the dimer rows toward the double steps. If there were no step-edge barrier at these double steps, the material should diffuse two layers downwards to fill up the remaining vacancies in the first layer. This should be followed by the second-layer islands extending to similar lengths as the first-layer islands before nucleation of the third layer sets in. Hence, in this case, the anisotropy in diffusion speed should lead to an efficient way to fill up the remaining vacancies in lower levels, and should result in excellent layerwise growth.

Instead of this scenario, we observe a slow accumulation of deep, elongated vacancies that are hardly overgrown. The boundaries of the vacancies are double steps or accumulations of even more steps. Already at a coverage of 3 ML, many of these vacancies are present [some vacancies are marked by V in Fig. 2(C)]. In addition, early nucleation of higher layer islands sets in well before completion of the lower layers, especially on those islands, that are terminated by multiple steps. An example of this is given in Fig. 2(D), where fifth-layer islands are present already at a total coverage of 3 ML. This suggests the existence of a step-edge barrier at double steps, which hampers downward mass transport in films thicker than 1 ML. Thus, during growth, more and more double or multiple steps are accumulated, downward mass transport is increasingly hampered, the growth front roughens progressively, and three-dimensional mounds are formed.

Having identified the kinetic cause for three-dimensional growth, a growth recipe may be given to grow flat films. The key point is to avoid the formation and accumulation of long double or multiple steps. This can be done by splitting up the deposition of each atomic layer into two stages with different deposition conditions, i.e., different kinetic situations. In the first stage, $\approx 80\%$ of an atomic layer is deposited at a low temperature (<370 K). In the second stage, deposition is continued at a higher temperature (e.g., 525 K), where the atomic layer is completed. Due to the low temperature in the first stage, the mobility of the deposited material is limited. Many small and irregular islands form. The density of steps is high and the film shows substantial lateral disorder and crystal imperfections, but no long steps are present. Downward mass transport, however, is still efficient due to the high density of single-layer steps, but due to the accumulation of crystal imperfections and antiphase boundaries, growth of thicker films at this low temperature would lead to amorphous films. To avoid this, during the second stage of growth the sample is heated to an elevated temperature, resulting in an annealing of the film and a reduction of crystal imperfections. The lateral order of dimer rows is achieved and more material from the second layer can diffuse downward to fill the lower layer. However, the structures on the surface resulting from annealing are much smaller than those after constant growth at this temperature. In particular, no tendency for the formation of long, straight steps is observed. Additionally, during the deposition of the remaining 20% of material for monolayer completion, a high mobility of the atoms on rather small islands allows an effective downward diffusion over the step edges of the islands and a filling of the remaining vacancies, identically to the procedures used during manipulated growth of metals[12] or during synchronized nucleation during homoepitaxy of Si(111).[13] As a result, a film is grown without long step edges and without the tendency for double-step formation, as illustrated in the inset of Fig 1(B).[14]

To show the advantage of ‘‘controlled growth,’’ we repeated this procedure to grow a 10-ML-thick film layer after layer, and compare the film morphology to those grown at constant deposition parameters. Figure 1(B) shows the morphology after controlled growth of a $\approx$10-ML film as seen with STM. Obviously, controlled growth by variation of growth parameters leads to a much flatter film morphology than with constant growth conditions [Fig. 1(A)], although the maximum temperature during growth of both films was the same. The surface of the film after controlled growth displays the 2×1 reconstruction (see the inset) with orientations of the dimer rows in registry with the substrate hinting at the good crystallinity of the film. Locally, only three atomic layers are exposed. By controlled growth, the root-mean-square roughness of the 10-ML films is largely reduced from ≈ 4.5 Å (constant deposition at 525 K) to ≈ 0.6 Å (two growth temperatures set to 370 and 525 K).

The distribution of material in the different atomic layers of the films also clearly shows the significant improvement of film flatness due to controlled growth. Figure 3 illustrates the distribution of the material as determined from STM scans. Constant growth at 525 K results in many exposed layers, and a distribution only slightly flatter than for ideal three-dimensional growth, i.e., complete absence of interlayer mass transport (Poisson growth).[15] This shows that downward mass transport is indeed strongly suppressed by multiple steps during conventional growth at this tempera-

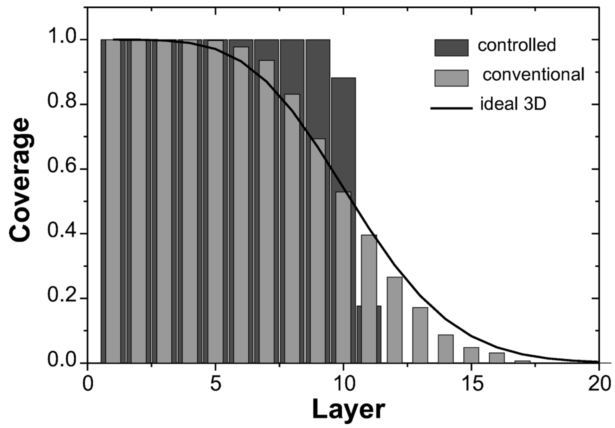

FIG. 3. Distribution of material into different atomic layers after conventional deposition at 525 K, and controlled deposition at 370/525 K of ≈10 ML Si. For comparison, the distribution after ideal three-dimensional growth is given as a solid line.

ture. In contrast to the very broad growth front of films grown under constant deposition parameters, controlled growth leads to an almost ideally flat surface. As can be seen from Fig. 3, only three layers are exposed at the surface, and the layer distribution has a very sharp edge, close to ideal two-dimensional growth. The ninth layer is completely filled and only some material is missing in the tenth layer, which is found in the eleventh layer. Hence, by controlling growth kinetics during deposition, downward mass transport is indeed enhanced greatly, and almost perfectly flat films can be produced at low temperatures. Note, however, that the Si films grown in this manner may well be heavily strained, as we did not detect indications of dislocations on our STM images. More detailed work which addresses the issues of bulk defects and strain by using diffraction techniques is currently in progress.

Since growth kinetics for all the three (2×1)-reconstructed systems Si/Si(100), Ge/Ge(100) and Ge/Si(100) shows the same characteristics of anisotropic diffusion and sticking combined with roughening during growth at low temperatures, for these systems the method of controlling the growth mode by variation of growth parameters should also allow the growth of nearly perfectly flat films. This then enables one to grow Si/Ge multilayers on the laboratory scale with sharp and flat interfaces at low temperatures, avoiding intermixing and strain-driven roughening. However, one has to keep in mind that especially uncovered strained films prepared in this way are in a metastable state which may not withstand conventional technological processes at temperatures above 800 K.[2] Alternative ways for variation of the growth parameters are available: the substrate may be heated, e.g., by a pulsed laser, or alternatively, strong modulation of the deposition rate by chopping the molecular beam may be chosen to control the growth mode. These procedures for growth manipulation may well be comparable to high-temperature surfactant-mediated growth, with the additional advantage of the complete absence of additives which may be incorporated into the growing film and act as undesired dopants.

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