Novel Strain-Induced Defect in Thin Molecular-Beam-Epitaxy Layers

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We have studied the morphology of thin epitaxial Ge films on Si(001). By terminating the surface with a monolayer of As during growth, Ge is forced to grow layer by layer, instead of the preferred mode, which is layer by layer for three monolayers, followed by islanding. In layer-by-layer growth, there are no nucleation sites for misfit dislocations to accommodate the 4% lattice mismatch. Instead, we observe by high-resolution transmission electron microscopy a novel strain-relief defect combining two $\Sigma 9$ boundaries and a twin. An estimate of the defect energy compares favorably with the energy of equivalent misfit dislocations.

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Strain and strain-relief mechanisms play an important role in determining the morphology and properties of epitaxial thin films. When the misfit between substrate and overlayer is completely absorbed by strain energy, the overlayer is called pseudomorphic. For large misfits and/or thick layers, some form of strain relief must occur. The formation of misfit dislocations and/or of twins is commonly observed, with dislocations being the most common. At the so-called "critical thickness,"[1] misfit dislocations become more favorable than overlayer strain. A review of the extensive theoretical and experimental literature on this subject is beyond the scope of this paper. Instead, we refer the reader to the original work by van der Merwe[1] and by Matthews and Blakeslee.[2,3] Surprisingly little work has been done on *how* the dislocations are introduced once the critical thickness is exceeded. Matthews and Blakeslee[2] proposed that dislocations are introduced by "looping" from the surface to the interface, but, to our knowledge, this mechanism has not been directly observed. For GaInAs on GaAs, Chilsholm and Kirchner[4] have shown that dislocations only form at the edges of the islands and that islands reaching down to the substrate still form when the critical thickness is exceeded, even after a uniform layer has already been established. For Ge/Si, it is well known that islands form after only three monolayers of Ge have been deposited, thus explaining the final microstructure, i.e., a completely relieved Ge layer, with dislocations relieving the misfit. The islanding is obviously energetically favorable, but, just as important, it is feasible because of the high surface mobility of Ge atoms on the Si surface. Recently, Copel, Reuter, and Tromp[5] have achieved layer-by-layer growth of Ge on Si(001) up to thicknesses of fifteen monolayers by saturating the Si surface dangling bonds with arsenic and suppressing island formation by rapid incorporation of the growing species in subsurface sites underneath the segregating As surface layer.

In this paper, we study the microstructure of films obtained in this manner, using transmission electron microscopy (TEM). Both planar view and cross-sectional samples have been observed, under high-resolution conditions. The films are found to be continuous and island free. The stress is relieved by the formation of thin defects along the $\langle 110 \rangle$ directions. The crystallography of this novel mode of strain relief is described. Possible explanations for its occurrence are discussed.

Films consisting of fifteen monolayers of germanium were deposited on Si(001) in the manner described in Ref. 5. Briefly, Si samples were cleaned by mild sputtering followed by a short flash at 1050 °C. Ge was deposited in UHV at 500 °C at rates of about 0.3 monolayer/min. The Si surface was passivated by one monolayer of As prior to growth, and an overpressure of As was supplied during Ge growth. A Si cap was deposited on the Ge film in order to avoid oxidation and loss of Ge. For comparison, a sample consisting of eight monolayers of Ge grown without As was also prepared. Samples were prepared for both planar view and cross-sectional TEM observation by mechanical thinning to about 50 μm, and then ion milling to electron transparency. Planar samples were observed on a Philips-430 microscope operating at 300 kV, cross-sectional samples were observed on a JEOL-4000 microscope operating at 400 kV.

Figure 1(a) shows the microstructure typical of eight monolayers of Ge grown on Si(001), without the help of a surfactant. Small islands are clearly seen. The presence of moiré fringes indicates that the islands are relaxed and have the lattice parameter of Ge (also shown on the diffraction pattern). Figure 1(b) shows the same sample in cross section. Dislocations can be identified by counting the number of lattice fringes on each side of the interface. Figure 1(c) shows a planar view of the sample grown using an As surfactant. The zone axis is $\langle 001 \rangle$, or exactly perpendicular to the substrate. The diffraction pattern shows weak elongated spots, along the $\langle 110 \rangle$ directions of the substrate, corresponding to the $\langle 111 \rangle$ spacing. The image reveals thin defects along $[\bar{1}10]$ and $[1\bar{1}0]$. The background of the image is featureless, revealing no dislocation or moiré fringes. Dark-field images on the extra spots (not shown) reveal that they are caused by the thin defects, which demonstrates that

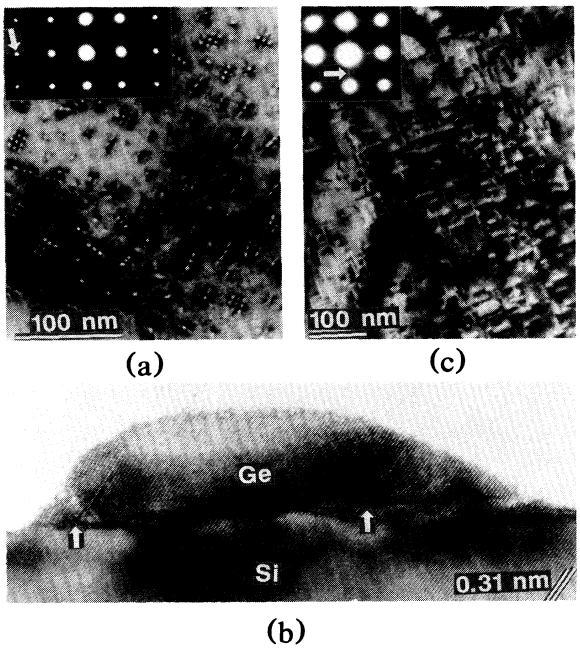


FIG. 1. (a) Planar view and diffraction pattern of eight monolayers of Ge grown on Si(001), without surfactant. The zone axis is ⟨001⟩. The arrow in the diffraction pattern indicates a region where the Ge and Si spacings can be distinguished from one another. (b) Same sample seen in cross section along the ⟨110⟩ axis. The arrows show the location of two dislocations at the Si/Ge interface. (c) Bright-field image and diffraction pattern of fifteen monolayers of Ge grown on Si(001), with As surfactant. The zone axis is ⟨001⟩. The arrow shows one of the extra spots attributed to the thin defects.

these correspond to very thin Ge platelets oriented so that the {111} planes are perpendicular to the substrate. This is further demonstrated in Figs. 2 and 3 which show high-resolution lattice images of the sample in cross section. Figure 2 shows a large area, where a continuous and uniform Ge layer is sandwiched between the substrate and the Si cap. One can actually count the Ge planes, and determine that the thickness is between fourteen and sixteen monolayers, as expected. The epitaxial Si cap is seen to be discontinuous: Si has grown epitaxially on the Ge that is epitaxially oriented, but no, or very little, growth has occurred over the defects (possibly Si has grown on top of the defect, but is amorphous and cannot be distinguished from the glue used for sample preparation). It is possible to count the number of fringes on each side of the interface for each epitaxial region and prove that there are no dislocations in these areas.

Crystallography of the defects.—The defect is shown in greater detail in Fig. 3(a). Multislice image simulations were used to arrive at the atomic structure of the defect. The atomic positions are shown superimposed on the micrograph in Fig. 3(b). The corresponding simulated image is shown in the inset.[6] The defect is built as follows [Fig. 3(c)]. It forms a wedge with boundaries near the $(\bar{2}21)$ and $(2\bar{2}1)$ planes of the substrate. These {221} boundaries are similar to Σ9 tilt boundaries, with one important distinction: In the present case, a twin exists inside the defect to join the two microcrystals generated by the presence of two Σ9 boundaries. This twin is visible on the micrograph, even though it only separates two crystals that are two {111} layers thick. Since this twin is a mirror plane, the {111} planes on each side of it have to be exactly parallel to the ⟨001⟩ axis. The angle between the $[\bar{1}12]$ (or the $[1\bar{1}2]$) direction and the normal to the surface is 35.26°, or 3.47° short of the 39.84° angle expected between the two sides of a true Σ9. Consequently, the defect has to be stressed in order to account for the 3.47° disclination angle. Despite the defect's small size and large disclination, the atomic configuration of the two boundaries fits remarkably well with calculated, lowest-energy Σ9 interfaces;[7] i.e., it is entirely formed by alternating five- and seven-atom rings. At no point is there any broken bond, and only minimal stretching of the lattices is required to fit the different orientations together. Thus, in spite of the complicated nature of this defect, it has a low total energy: It is bounded by two low-energy boundaries, the twin is known to have very little extra energy, and, where it meets the substrate, the defect has narrowed down to a point, so that no extra interfacial energy is introduced. We are presenting only one such defect, but several have been observed at high resolution and all have been analyzed in the same way.

Strain relaxation.—Each pair of {111} planes parallel

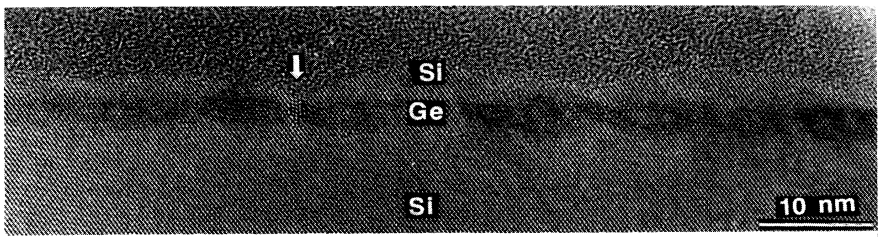
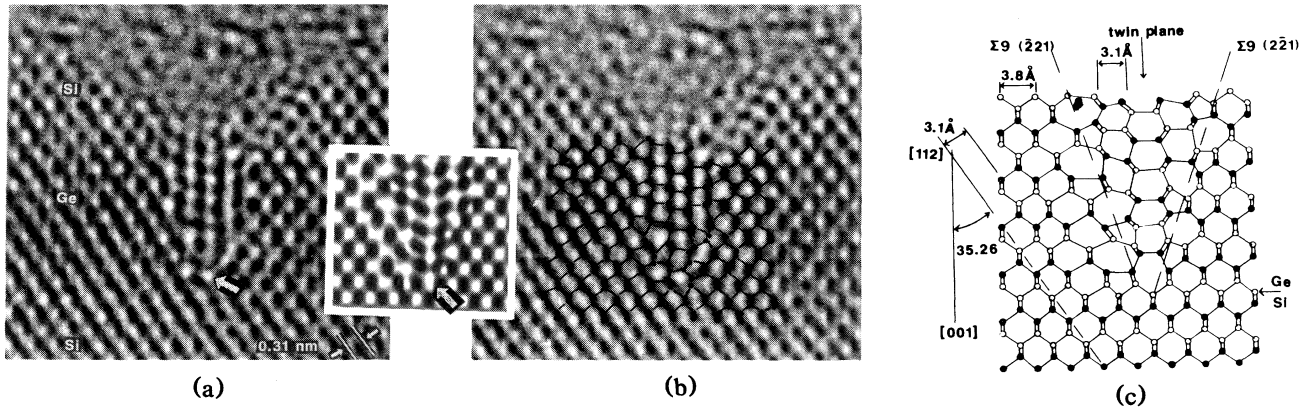


FIG. 2. Cross-sectional view of the sample presented in Fig. 1(c). The arrow shows one defect.



(a) (b) (c)

FIG. 3. (a) Detail of one defect. (b) Same defect, with atomic position superimposed (black-atoms assumption). (c) Atomic model of the defect. Inset between (a) and (b): Simulated image. The arrows on (a) and in the inset show the same atomic position, so that comparison between simulation and image can easily be done.

to the [001] bulk axis gives rise to a total shear of

$$a(1/\sqrt{2}-1/\sqrt{3})=0.1835a/\sqrt{2},$$

where a is the lattice parameter of Si. Thus, in order to account for a misfit of 4%, about 22% (4/18.35) of all the {111} planes have to be tilted. If, as observed, on average each defect is 4.5 planes thick, one defect every 85 Å is needed to completely relieve the strain. Figure 1(c) shows that the distance between defects is about 250 Å; thus only about one-third of the misfit has been relieved. It is interesting to note that, since the defects are V shaped, they become wider as the film grows, thus accommodating a larger portion of the misfit. Eventually, all of the misfit would be relieved, without the need to create more defects, when the defects reach a width of twelve planes, at a film thickness of about 53 Å. Since the width of the defect increases with thickness, the lattice parameter changes continuously through the Ge film, with no discontinuity at the Si/Ge interface, thus explaining the absence of moiré fringes.

This is the first reported observation of such defects in epitaxial thin films. The novel defect is the result of an unusual kind of growth: The Ge film has been forced to grow layer by layer, instead of islanding, which is its preferred mode of growth. With increasing thickness, there is a very large driving force to relieve the strain. But, since the growth occurs layer by layer, the nucleation of dislocations at island edges, as observed by Chisholm and Kirchner,[4] is inhibited. Thus, the film continues to grow until the strain is so high that the observed defects are created catastrophically throughout the film. The "catastrophic" nature of the stress-relief process is demonstrated by the fact that the defects are small in size, uniformly distributed, and, most importantly, completely disconnected, or independent from one another. We note that the formation of these defects appears to be similar to the martensitic transformation, in which no diffusion is needed, only local atomic rearrangement. During "normal" stress relief the dislocations form networks, where each dislocation goes from one end of the sample to the other (some of them do thread to the surface; see, for example, Ref. 8). Our results indicate that, contrary to what was proposed by Matthews and Blakeslee,[2] misfit dislocations are not generated by looping from the surface of a uniformly growing thin film, but need well defined nucleation sites from which they may migrate along the interface (e.g., islands, steps, dirt, etc.). The defects presented here generate a shear similar to deformation twining. This shear is significantly larger than is generated by a regular twin, since it replaces 3.8 Å with 3.1 Å [see Fig. 3(c)].

The energy of one defect can be estimated at follows: The energy of the Σ9 boundary per unit area was calculated[9] to be 0.02 eV/Å^2. The length of boundary per defect is $3h/\sqrt{2}$, where h is the thickness of the film. If we neglect the energy introduced by the presence of the twin, which is negligible compared to the energy of the two Σ9 boundaries, as well as the elastic energy associated with the disclination (the "missing" 3.47°), the energy per unit cell in the [1̄10] direction and for the thickness of the present film is 3.4 eV, or 0.44 eV/Å. For comparison, the energy of an edge misfit dislocation in this system would be about 0.556 eV/Å [using $\mu b^2/4\pi(1-\nu)$, where μ and ν are the rigidity and Poisson's ratio, respectively, and b is the Burger's vector, with the average elastic constant of Si and Ge used for the calculation[10]]. As mentioned before, one defect every 85 Å would be necessary to completely relieve the strain, while one dislocation every 95 Å would be necessary; thus, as a first approximation, the energy values can be compared directly. These values should only be used as orders of magnitude because the calculation of the energy of the Σ9 boundary was done for Si and not Ge, this is not an exact Σ9 boundary, the energy of the twin and of the

dislocation were neglected, and, finally, the interaction between the dislocations was neglected. Nonetheless, these estimates certainly indicate that the energies of the defect and of an equivalent misfit dislocation are comparable, so that the formation of the defect should not be surprising. On the other hand, contrary to dislocations, the energy of this type of defect would increase as the film grows and, for larger thicknesses, become significantly less favorable than dislocations. However, once established, this microstructure should be quite stable.

In summary, we have described the microstructure of Ge thin films that have been forced to grow layer by layer. We have reported a novel defect to accommodate the misfit between Si and Ge. The atomic crystallography of the defect has been given and consists of two $\Sigma 9$ boundaries, forming a V with its tip at the Si/Ge interface, and creating two microcrystals related to each other by a simple twin. Estimates of the energetics of this defect compare favorably with those for a misfit dislocation. Perhaps the most important conclusion is that suppression of island formation retards or even prevents the nucleation of simple misfit dislocations and gives rise to the formation of defects which are not observed under conventional growth conditions.

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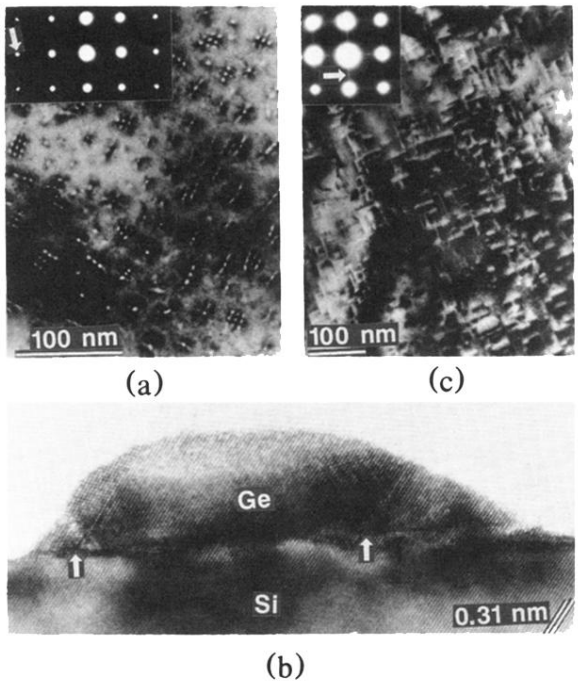

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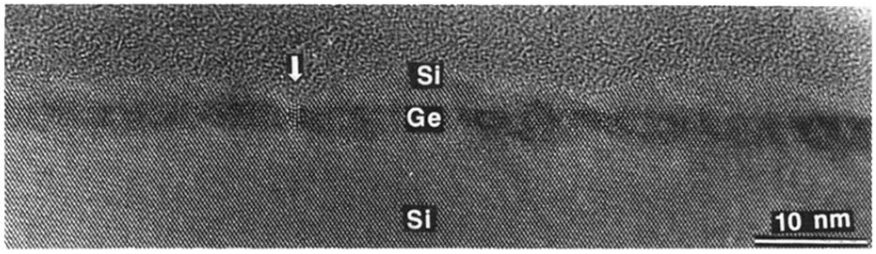

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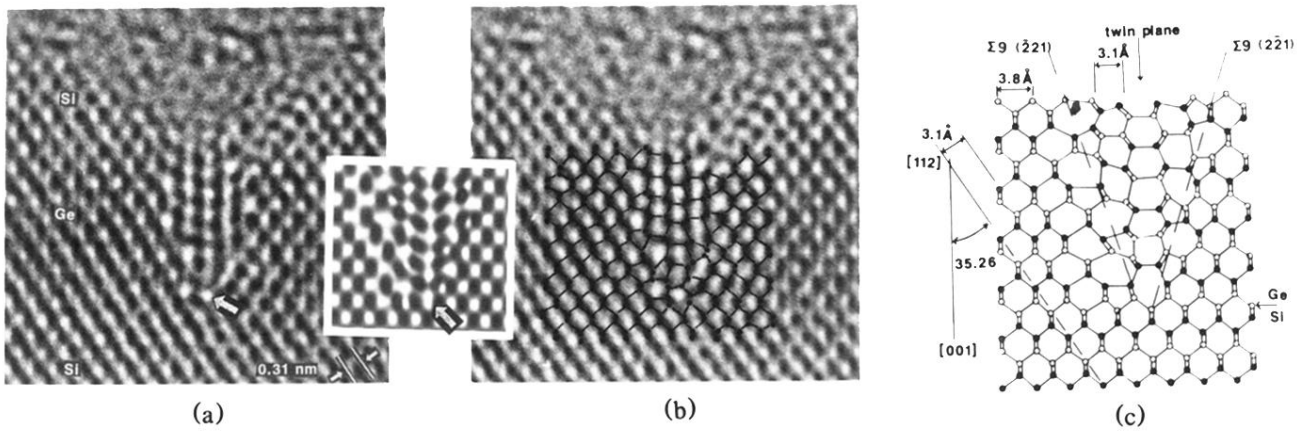

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