Growth Morphology and the Equilibrium Shape: The Role of "Surfactants" in Ge/Si Island Formation

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(Received 2 September 1992)

Surface energy *anisotropy*, as opposed to surface energy, is shown to influence changes of growth mode in Ge/Si by "surfactant" impurities. By annealing thin Ge/Si films, we find the equilibrium island shape, and hence the surface energy anisotropy; radical changes in shape are seen for impurity-terminated surfaces: Ge:Sb enhances (100) facets compared to clean Ge and Ge:In favors {311}. Thus Sb impurities favor large flat islands which would lead to earlier island coalescence and can aid planar (100) growth, while In (though otherwise a good "surfactant") leaves the film faceted. Island suppression by a "morphactant" thus depends on enhanced faceting onto (100), as well as reduced diffusion.

PACS numbers: 68.55.Bd, 61.16.Bg

The use of impurities to control epitaxial growth mode has been widely discussed recently, either as "surfactant mediated growth" (SMG) [1–4] or as "segregant assisted growth" (SAG) [5,6]. The most spectacular of the reported effects is the total suppression of island formation in Ge/Si molecular beam epitaxy (MBE) by predeposition of a monolayer coverage of As or Sb [1,2]. One explanation for this effect [1] is the action of the impurity as a surfactant [7]: By lowering surface energy, As or Sb can force Ge to wet Si. The primary problem with this view lies in our detailed understanding of Ge/Si growth [8,9]. Pure Ge has a lower surface energy than Si, so elemental Ge/Si growth already results in wetting. ("Surfactant" behavior has also been observed in other systems where the epilayer wets the substrate [10].) As expected for lattice-mismatched epitaxy, Stranski-Krastanow island formation occurs at a later stage in growth due to strain considerations, rather than surface energy. Alternatively, we can view islands in a strained system as arising from the large interface energy of a dislocated interface. What, then, can be the effect of a surfactant on this scenario? Island formation is driven by the strain relaxation that can be attained through either plastic or elastic deformation around an island [11]. While this process can be impeded kinetically by the suppression of surface diffusion, the only energetic term opposing island formation is surface tension: Islanding increases surface area. More precisely, in a Stranski-Krastanow system with fixed interface energy (from misfit dislocations), reducing surface energy will *increase* the contact angle at the edge of a dislocated island. Thus use of a surfactant impurity in a materials system where the epilayer wets the substrate may either control islanding kinetically by suppressing diffusion, or enhance islanding energetically.

Until recently, it thus appeared likely that surfactant growth (at least for Ge/Si) was equivalent to reducing the surface diffusion: Beautiful data now exist for a mechanism whereby As suppresses Ge diffusion on Si [12]. (Although it is sometimes argued [12] that kinetic suppression is a consequence of lowered surface energy,

there is no *a priori* link between diffusion and surface energy.) Even for the pure Ge/Si system diffusion can be sufficiently reduced (by growing at 200 °C) for island formation to become negligible [13]. Recently, however, it has been reported that solid-phase epitaxy of a Ge film heavily doped with Sb can lead initially to roughness, but subsequent annealing smooths this rough surface [14]. This surprising result appears to suggest that the impurity favors an equilibrium configuration of a planar film. Here, we investigate the link between impurities and the equilibrium configuration by postgrowth annealing under an impurity flux of H, In, or Sb (as opposed to the predeposition of impurity on Si to modify subsequent growth): The observed equilibrium shapes indeed suggest that modification of the surface energy *anisotropy* plays an important part in the action of surfactants (or "morphactants").

Growth and *in situ* annealing were carried out in a conventional Si MBE chamber with a base pressure $\approx 10^{-10}$ Torr, using Si and Ge *e* guns, Knudsen cells for Sb and In deposition, and a W filament for atomic H (deuterium) dosing [15]. Sources were calibrated by measuring surface coverage using Rutherford backscattering spectrometry (RBS) for Sb and In, and secondary ion mass spectroscopy for deuterium. Si(100) wafers were cleaned prior to Ge epitaxy by an HF dip, H desorption, and deposition of a 100–500 Å Si buffer at ≈ 600 °C. Thin [5–15 monolayer (ML)] Ge films were then deposited at temperatures ranging from 400 to 600 °C, and subjected to anneals of 1–10 h at 400 –700 °C in impurity beams of 0.01–0.1 ML/s (i.e., a large excess of impurity) to reach an equilibrium shape. Morphologies arising from both impurity anneals (after island formation) and surfactant growth (predeposition of impurity) were studied. Islands were studied using transmission electron microscopy (TEM) of both (010) and (011) cross sections [and (100) plan views] prepared by mechanical polishing to ≈ 80 μm and Ar-ion milling to perforation. The square {110} morphology seen in plan view indicated that {hkk} facets dominated the shape, so

that (011) cross sections should be used to determine the relative energy of the important facets. Island shapes were studied in cross section on small ($\approx$ 100–500 Å thick, wide) electron-transparent islands in regions where they were protected from ion beam sputtering by a relatively thick Si substrate. Given an equilibrium shape, the Wulff construction [16,17] allows us to extract a plot of surface energy as a function of angle $\gamma(\theta)$. Since for all the systems studied here the shapes lacked abrupt cusps [16] (i.e., all islands were smooth), measurements of the radius of the island at 2° spacings are directly related to the relative values of $\gamma(\theta)$. The only manner in which this geometric construction differs from previous studies of surface energy anisotropy in isolated particles [15] is the definition of the nominal "center of mass" (Wulff point) of the island, which we determined by the intersection of the normal bisectors of the three visible facets [the (100) and two {311}'s], as opposed to the bisectors of four faces used to determine complete 3D $\gamma(\theta)$ plots in the previous work.

While the experiments appear trivial, the achievement of equilibrium shape poses some problems. H, In, and Sb all act to suppress island nucleation kinetically; at 500 °C the characteristic island size and spacing is reduced 3-fold, 20-fold, and 100-fold with respect to clean Ge for surfaces with predeposited H, In, and Sb. Equilibrating island distributions is thus problematical. Note that even Sb does not prohibit islanding when we use a post-growth anneal at the growth temperature (under otherwise identical conditions to those specified in earlier papers), but greatly slows this process so that at typical deposition rates it may not be observed. The criteria used to define equilibrium are that all islands approach the same shape as annealing proceeds, with small islands reaching this shape first, and that the final shape should be size independent (these criteria rule out kinetic mechanisms for attaining uniformity of shape [16,17]). A wide variety of deposition sequences were used (predeposition of impurity, low-temperature layer-by-layer growth of pure Ge, and a variety of post-growth anneals), but uniform shapes
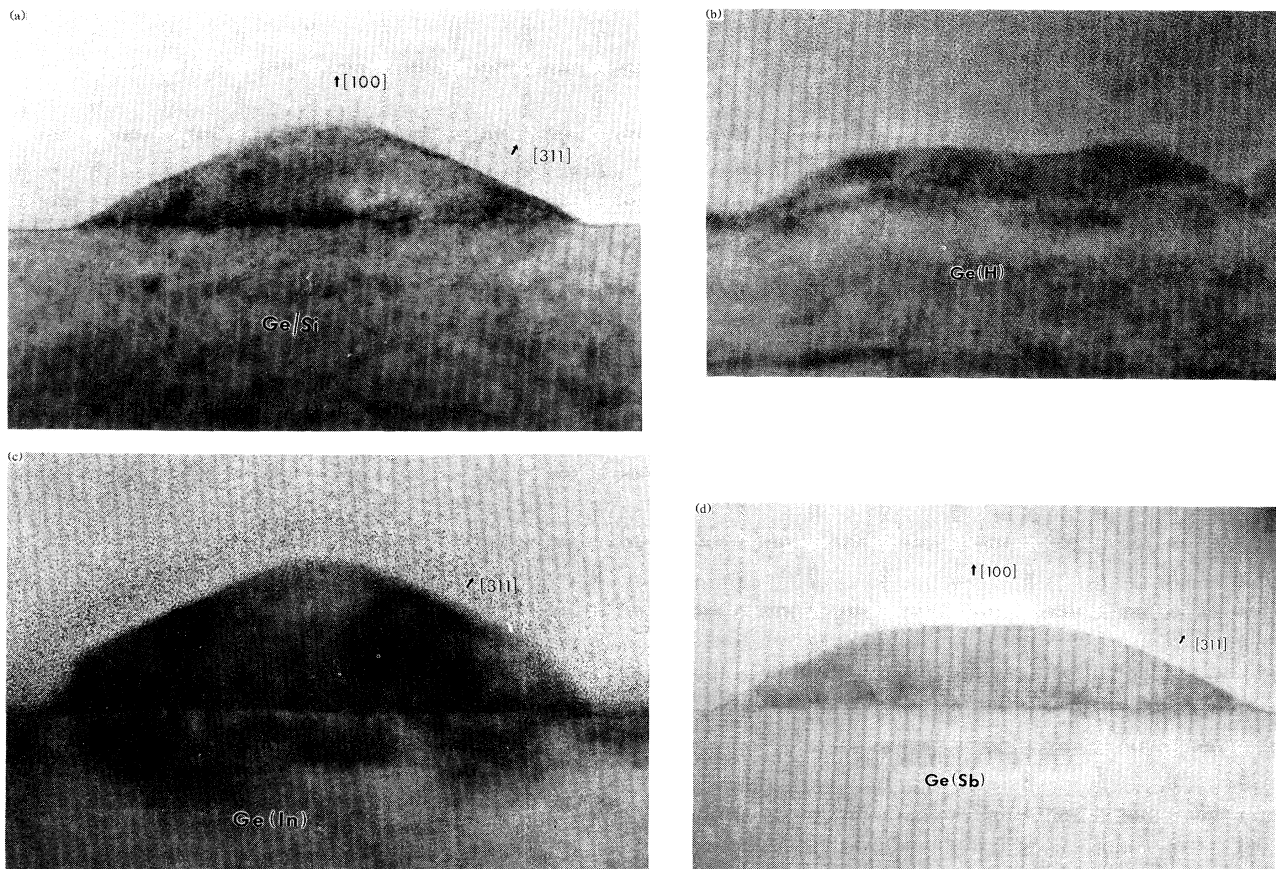

FIG. 1. Typical island morphologies seen in clean Ge/Si and following anneals in H, In, and Sb. The island morphology for Ge, Ge:In, and Ge:Sb was identical everywhere, so the forms seen here are the equilibrium shape of Ge in the presence of these impurities. Note the very strong variation of island shape with impurity, and note that the impurity (Sb) that behaves as a good "surfactant" on (100) has greatly enhanced the (100) facet on the equilibrium island.

were most easily achieved by high-temperature (500 °C) deposition of clean Ge (so that island formation is initiated) at relatively low coverages ($\approx$ 5–8 ML) and prolonged annealing (1–10 h) under substantial impurity fluxes as close to the desorption temperature as possible [700 °C, 400 °C, and 500 °C (0.8 to 0.6 of the melting point) for Sb, In, and H, respectively]. All annealed islands had a high density of interfacial dislocations; some had a few threading dislocations or stacking faults. Residual strains calculated from dislocation spacings were small, and islands with and without threading defects had identical shapes.

Figure 1 shows typical shapes for Ge islands given post-growth anneals in H, In, and Sb, with a control for comparison. Even for the longest (5 h) anneals close to the H desorption temperature, annealing in H did not appear to produce regular shapes, but showed variable unfaceted shapes with a rough back Ge/Si interface. This behavior is not inconsistent with the effect expected for a simple surfactant: By lowering all surface energies irrespective of orientation, a surfactant merely reduces the energetic barriers (facet and step energies) that oppose roughening and islanding. It is also possible that the microstructure observed is linked to desorption of H from Ge regions while the Si surface remains H terminated. [H begins to desorb from Ge at 350 °C [18]. We do not, however, observe significant H etching of Ge. Annealing of clean (100) Si in the atomic H beam at these temperatures does not roughen the surface.] Since uniform size-invariant shapes were not generated the morphology is presumably dominated by kinetics rather than energetics and the film lies far from the equilibrium shape.

Sb, In, and clean surfaces all showed uniform island shape and strong faceting, with distinctive differences between the differently terminated surfaces. The shapes shown in Fig. 1 are not merely representative, but indistinguishable from island to island. (Because of the long anneal time, high uniformity, and size independence of the shapes we believe that these shapes are equilibrium and are not affected by relative diffusion on different facets.) By inspection of Fig. 1 the (100) facet is small but measurable for clean Ge, much larger for Ge:Sb, and negligible for Ge:In. All three island shapes are dominated by {311} facets. This immediately suggests a possible role for impurities in reducing islanding not through lowering of absolute surface energy, but through stabilizing a particular facet [in this case the (100)] with respect to nearby orientations [stepped (100) and {311}]. Thus Sb works well as a surfactant partly because the reduced diffusion kinetically suppresses island formation, but also because the increased (100) faceting of islands strongly favors early island coalescence and ideal (100) planar growth after coalescence. Since the additional effect depends on surface energy *anisotropy*, and absolute surface energy is irrelevant to the suppression of island morphology, Sb might be better labeled a *morphactant* for

Ge/Si(100) planar growth. This (as will be seen more explicitly later) is a consequence of two related features: the reduced ratio $\gamma(100)/\gamma\{311\}$ and the increased step energy $d\gamma/d\theta$ at (100). (It should be noted that because of reduced diffusion, the island shape seen with Sb was somewhat growth dependent, with preformed islands evolving towards flatter shapes, and flat layers evolving towards higher islands, even at the end of the longest anneals. The shape shown in Fig. 1 is typical of the former growth technique: The conclusions drawn subsequently will tend therefore to be conservative in assessing the *degree* to which Sb affects the equilibrium shape.) The Ge:In islands also highlight a potential problem in using a surfactant in a system that already wets. The increased contact angle ($\approx$ 55°, as opposed to $\approx$ 25° for Ge and Ge:Sb) suggests that this system may now be in a Volmer-Weber growth mode, i.e., Ge:In no longer wets Si:In. Island formation was observed for Ge/Si(100):In at Ge coverages down to 0.8 monolayer, confirming that for this system the addition of In converts the growth mode from Stranski-Krastanow to Volmer-Weber. This is still perfectly consistent with In acting as a surfactant (in the true sense that it lowers the absolute surface energy of both Si and Ge) provided that the Si γ is lowered by more than that of Ge, so that while $\gamma(\text{Ge}(100))$ < $\gamma(\text{Si}(100))$, $\gamma(\text{Ge}(100):\text{In}) > \gamma(\text{Si}(100):\text{In})$.

In Fig. 2 we show the surface energy plots $\gamma(\theta)$ extracted by the Wulff construction from the equilibrium shapes in Fig. 1. For each plot the island radius was measured as a function of angle (averaged over several islands) with respect to the island center. Although Fig. 2 represents the first reported measurements of the equilibrium shape of Ge islands, the values of relative surface energies seen here should not be taken too seriously. This
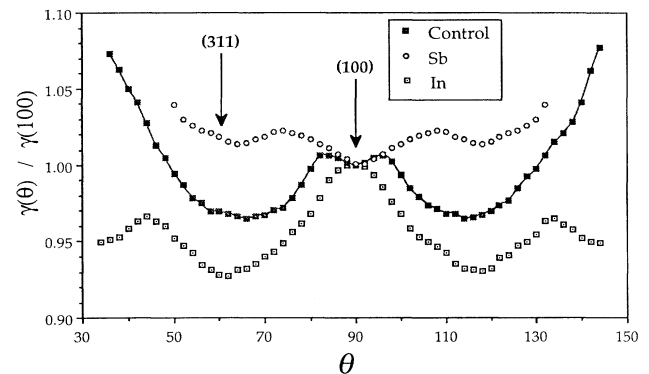

FIG. 2. $\gamma(\theta)$ plots: surface energy as a function of orientation near (100) (90°) extracted using the Wulff construction from islands like those in Fig. 1 for Ge, Ge:In, and Ge:Sb. Each curve represents an average over several islands. Note again the *relative* stabilization of the (100) facet with respect to {311} using Sb and the destabilization with In. All curves are normalized to $\gamma(100) = 1$, so *absolute* surface energies (surfactant behavior) is irrelevant here.

is because surface tension effects at the island edge will tend to skew all these plots towards lower apparent energy at higher angles from the surface normal ($\theta = 90°$ at [100]). Thus the transition from convex to concave shape at the island edge increases the size of the {311} facets relative to the true equilibrium shape, and thus lowers the apparent energy of the {311} cusps [relative to (100)] in Fig. 2. The deviations in island shape on a given sample can give rise to a $\approx 10\%$ change in the ratios of surface energy found in Fig. 2. The main purpose of the measurements in Fig. 2 is to show the role of surface energy anisotropy in affecting morphology. In Fig. 1 it is already apparent that even in equilibrium (i.e., in the absence of any effect due to the reduced diffusion) Ge:Sb does not "ball up" as dramatically as either clean Ge or Ge:In. In some sense the degree of islanding seen is a consequence of the height/width ratio of the equilibrium island. Figure 2 explicitly relates this increased apparent "wetting" to a change in $\gamma(\theta)$ whereby (relative to clean Ge) Ge:Sb has a decreased ratio $\gamma(100)/\gamma(311)$, while for Ge:In this ratio has increased. We could say that Sb acts as a morphactant for growth on (100) because (in comparison to the clean system) it favors the (100) facet over {311} facets and other forms of morphology. The result also seems to have implications for the standard surfactant growth. Growth morphology arises from a combination of energetics and kinetics: While diffusion mechanisms [12] may be important at short times, it is clear that effects arising from equilibrium morphology discussed here must always dominate in the long-time limit. Hence, while the kinetic suppression of islanding [12] is undoubtedly important, the anisotropy (morphactant) appears to be an additional important process, without which we cannot explain either the transition from islands to layer-by-layer morphology [14] or the failure of In surfactant to suppress islanding.

In summary, we have shown that control of the morphology of grown films by impurities may at least in part be attributed to changes in the surface energy anisotropy, and that this effect appears to be more important than lowering of absolute surface energy. Understanding the role of the equilibrium shape in altering the growth mode appears to be important for the successful use of mor-phactants to control the growth mode.

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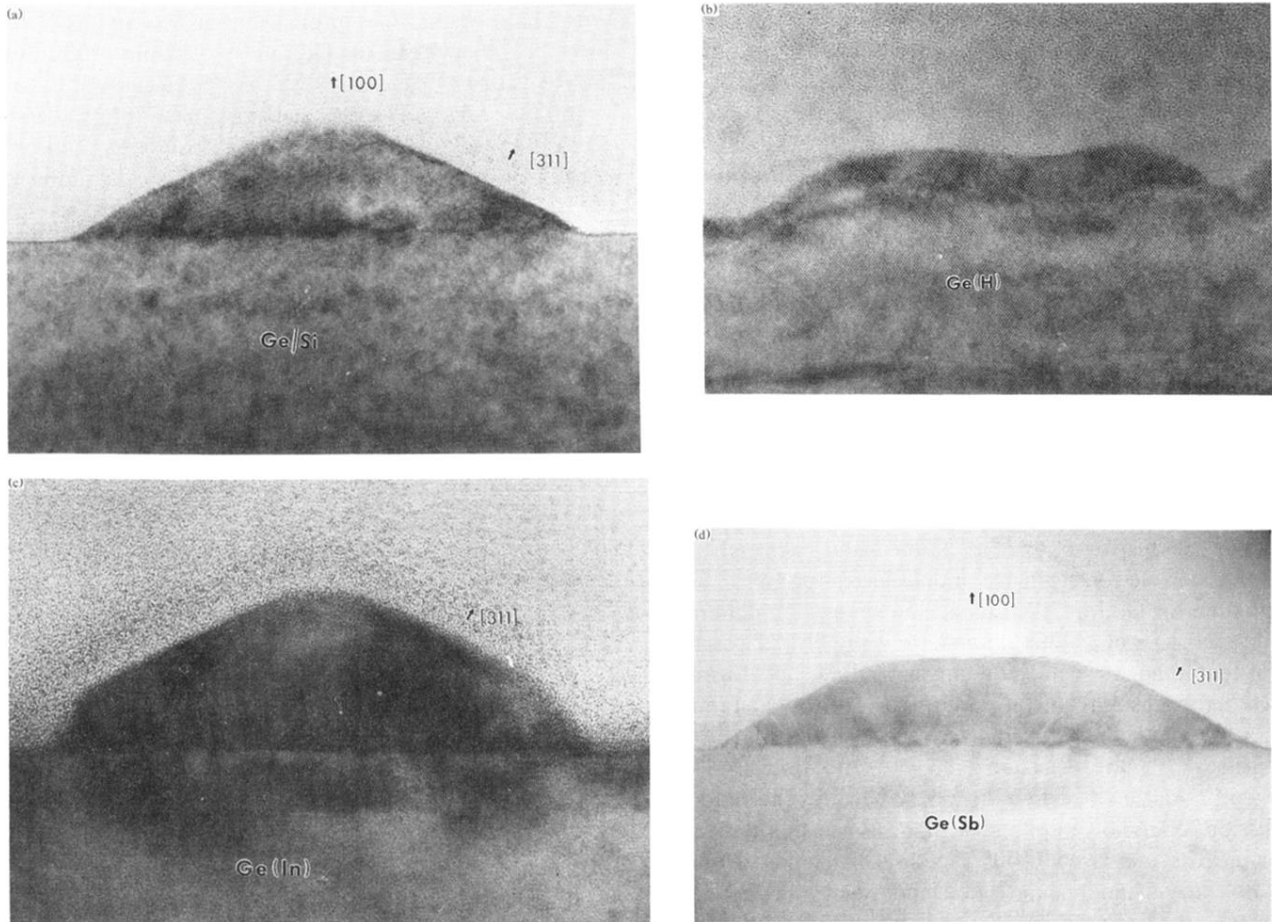[18] L. Surnev, Surf. Sci. **138**, 40 (1984).

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