Surfactants in Epitaxial Growth

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We have investigated the role of surface-active species (surfactants) in heteroepitaxial crystal growth. In general, the growth mode is determined by the balance between surface, interface, and film free energies. Thus, if A wets B, B will not wet A. Any attempt at growing an $A/B/A$ heterostructure must overcome this fundamental obstacle. We propose the use of a segregating surfactant to reduce the surface free energies of A and B and suppress island formation, as demonstrated in the growth of Si/Ge/Si(001) with a monolayer of As. Control of growth by manipulation of surface energetics provides a new avenue to achieve high-quality man-made microstructures against thermodynamic odds.

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A primary concern in obtaining good crystal growth by molecular-beam epitaxy (MBE) or other related vapor-phase techniques is the growth mode of the film. Both lattice strain and surface free energy help determine whether a film undergoes layer-by-layer growth (Frank–Van der Merwe), islanding (Volmer-Weber), or layer-by-layer growth followed by islanding (Stranski-Krastanov). Deliberate introduction of a surfactant that alters the surface free energy can change the growth mode of a film. We will demonstrate this for the growth of Ge on Si(001) and Si on Ge/Si(001) and show the importance of an As surfactant layer.

Theoretical models of epitaxial growth suggest that the growth model is determined by the free energy of the substrate surface (σ_s), the interface free energy (σ_i), and the surface free energy of the heteroepitaxial layer (σ_f), neglecting the strain energy of the film. The inequality

$$\sigma_s > \sigma_f + \sigma_i$$

sets the condition for the epitaxial film to wet the substrate. In this case, Frank–Van der Merwe growth may occur. If the inequality has the opposite sign, one usually obtains Volmer-Weber growth, i.e., no wetting of the substrate. The Stranski-Krastanov growth generally occurs when there is wetting of the substrate but the overlayer strain is unfavorable, or when there is the added complication of interface mixing and/or surface reconstruction, such as in Ag/Si(111). This work will not address the latter.

For two elements, A and B, one of the two species must, by necessity, have a lower surface free energy. Consequently, if A can be grown on B in either a Frank–Van der Merwe or Stranski-Krastanov mode, then B will grow on A in a Volmer-Weber mode. This imposes a significant barrier to the growth of embedded layers; if the embedded film grows well, then the capping layer does not. For the case of Si and Ge, Ge grows on Si(001) in a Stranski-Krastanov mode,[1–5] and Si grows on both Ge(001) and Ge/Si(001) in a Volmer-Weber mode.[4] This is a result of the above inequality, where Ge has a lower surface free energy than Si, and σ_i may be considered insignificant. Any attempt to grow a Si-Ge superlattice must overcome the fundamental limitations imposed by the growth modes of the constituents. Indeed, studies of Si/Ge/Si quantum-well structures have observed islanding of Si capping layers as well as severe interdiffusion effects, both resulting from surface energetics.[6,7]

A substantial modification of the film growth may be obtained by introducing a third element which lowers the surface free energy of both Ge and Si. In this case, segregation of the surfactant is strongly favored during growth. As a result, islanding of the film will be kinetically inhibited. We have achieved this by passivating the Si(001) surface with 1 monolayer (ML) of As prior to growth. The As layer, which contains one extra valence electron per surface atom, fills the dangling bonds which normally occur on the clean Si(001) and Ge(001) surfaces, thereby creating a stable termination.[8] We note that both clean Si(001) and As-capped Si(001) have (1×2) unit cells caused by formation of Si or As dimers. The difference between growth on the clean and As-capped surfaces is not due to the presence or absence of a reconstruction, but to the energetically favored filling of dangling bonds. By using the As-passivated surface as a stage for MBE growth, we are able to alter the growth mode of an epitaxial layer to induce wetting of the substrate. Since As segregates to the surface during growth, the structure itself incorporates relatively small quantities of As.

We have performed extensive energy-minimization calculations in the framework of local-density-functional theory using norm-conserving pseudopotentials and a large plane-wave basis set to obtain estimates of the surface energetics of the growth process. A number of possible configurations, including Ge layers on As-capped as well as clean Si(001) surfaces were considered. We find that the energy difference between ... Si/Si/Ge and ... Si/Ge/Si or ... Si/Si/Ge/As and ... Si/Ge/Si/As is

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relatively small (0.13 eV and −0.12 eV per dimer, respectively). However, the energy difference between ... Si/Ge/Si/As and ... Si/Ge/As/Si or ... Si/Ge/As and ... Si/As/Ge is very large (2.3 eV and 1.7 eV per dimer, respectively), strongly favoring surface termination with As. Therefore, Si and Ge atoms that adhere to the As-capped surface during growth will rapidly exchange sites with the As atoms and incorporate into subsurface sites. This leads to a large decrease in the surface mobility of the growing species, consequently restricting both islanding and interdiffusion between Si and Ge. Similar attempts to influence the growth of epitaxial metal layers have been reported.[9] However, success was limited because the adsorbate preferentially lowered either σ_s or σ_f, resulting in incorporation of the surfactant and a failure to embed the heterolayer. In the present work, we have used a dopant that reduces both σ_s and σ_f, giving extremely efficient segregation of the surfactant.

Experimental tests of the effect of a surfactant were obtained by *in situ* examination with medium-energy ion scattering (MEIS). Samples were prepared in an MBE system directly coupled to an ultrahigh vacuum MEIS chamber with facilities for x-ray photoemission spectroscopy (XPS). The MEIS system has already been described in detail,[10] and a review of the experimental technique can be found in the literature.[11] In brief, the technique consists of high-resolution Rutherford backscattering using an electrostatic energy analyzer to resolve the backscattered ions. Channeling spectra were taken with 100-keV He^+ incident in the [11$\bar{1}$] direction. Random spectra were obtained by an azimuthal rotation of 11° about the sample normal. Coverages were measured by MEIS with an estimated accuracy of ±5%.

Clean Si(001) samples (SEH, 10 mΩ cm) were prepared by a recipe of degassing followed by mild sputtering and a short flash to 1050 °C to remove the native oxide.[12] Depositions took place at a sample temperature of 500 °C, with both Si and Ge growth rates of ≃0.3 ML/min. Studies of Sb incorporation in Si(001) conclude that at temperatures of ≃500 °C, growth rates as high as 0.2 ML/sec can be sustained before surface segregation of the dopant species becomes kinetically limited.[13] Thus, growth rates could be significantly higher than used in this study without causing unacceptable depletion of the surfactant due to incorporation. Furthermore, because our growth rates are lower than those used in typical MBE, we have a *more* pronounced tendency for islanding and interdiffusion. This suggests that the procedures found effective in this study would certainly prove sufficient at more realistic growth rates.

Evidence of the effectiveness of a surfactant in controlling film growth may be seen in the growth of Ge on Si(001). Initial studies were done *without* the surfactant. Backscattering spectra for a nonchanneling geometry with the analyzer positioned at a 55° scattering angle exhibit a peak at 96 keV due to surface Ge, with a low background due to islands [Fig. 1(a)]. (Backscattering from Si occurs at much lower energy due to the effect of target mass on the scattering kinematics.) With increasing Ge coverage, the surface concentration saturates at 3 ML, and additional intensity is only apparent in the islanded Ge. Examination of the samples with transmission electron microscopy (TEM) confirmed the presence of Ge islands ≃100 Å thick. All of these results are compatible with Stranski-Krastanov growth, as observed in other investigations.[1-5]

In contrast, Ge films grown with a constant flux of As during deposition show an altogether different morphology. We have grown films as thick as 15 ML, the maximum thickness examined, with layer-by-layer growth and minimum yields (χ_{min}) of less than 5%. Both chan-

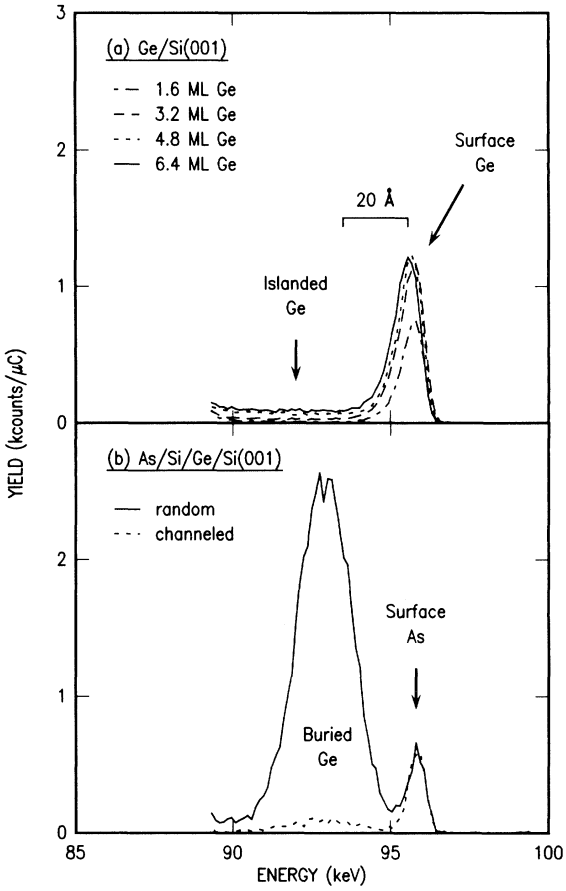

FIG. 1. Ion backscattering spectra for Ge/Si(001) films grown at 500 °C. (a) Deposition without a surfactant results in islanding of Ge after ≃3 ML, indicated by the tail on the Ge backscatter peak. Spectra were taken with a randomly incident ion beam. (b) Films grown with an As passivation layer and capped with 16 ML of Si show no sign of islanding. A 15-ML Ge film is shown for both random and channeling geometries.

neling and random spectra are shown in Fig. 1(b) for Ge films capped with 16 ML of Si. Neither the saturation in the surface concentration nor the background from islanding characteristic of Stranski-Krastanov growth are apparent. At this point a word of caution must be interjected. Using a surfactant can alter the growth mode of a film, but it does not relieve the presence of strain. Despite the excellent χ_{min} of the Ge layer, substantial defects occur to relieve the 4% lattice mismatch.[14] Next, we will examine Si growth on a 1.5-ML embedded Ge layer, where strain is expected to play an insignificant role, and the surfactant-mediated growth is quite low in defects.

Surface passivation with As has a profound effect on the subsequent growth of Si on a Ge layer. In Fig. 2(a), we show a 1.5-ML film of Ge deposited at 500 °C on a clean Si(001) sample that has not been predosed with As. The spectra were taken with the analyzer positioned at a 43° scattering angle. The Ge backscatter peak is centered at 96 keV, indicating that the Ge is confined to the surface region. We then proceed to deposit 8 ML of Si on the sample [Fig. 2(b)]. The channeling spectrum is quite similar to that seen before the deposition. The Ge surface peak has diminished, but there is still a significant quantity of surface Ge. The random spectrum is quite unlike what was seen before the Si deposition. There is now a long tail on the Ge peak, due to Ge that is buried underneath epitaxial Si islands.

In backscattering geometries less surface sensitive than shown in Fig. 2, we can observe some of the Ge buried under as much as ≃40 Å of Si, which is far too thick to be caused by intermixing in an 8-ML Si cap. Furthermore, studies of Ge epitaxy on Si(001) and Si(111) conclude that there is little diffusion of Ge into the Si substrate.[4,5] We can therefore conclude that our results are the product of Si islanding, as opposed to solely interdiffusion. A second point that can be made is that the Si cap is grown on a Si lattice and does not undergo significant strain. This suggests that the Volmer-Weber growth of the cap is not due to lattice misfit, but due to the energetics of the surface and interface.

Let us now examine growth using a surfactant. If we repeat the procedure used to grow the islanded sample, but use a sample that has been passivated with 1 ML of As at 500 °C prior to deposition, the Ge is buried under the Si cap [Fig. 2(c)]. In the channeling spectrum (dotted curve) there is a Si surface peak and an As surface peak at 91 and 96 keV, respectively. Although As and

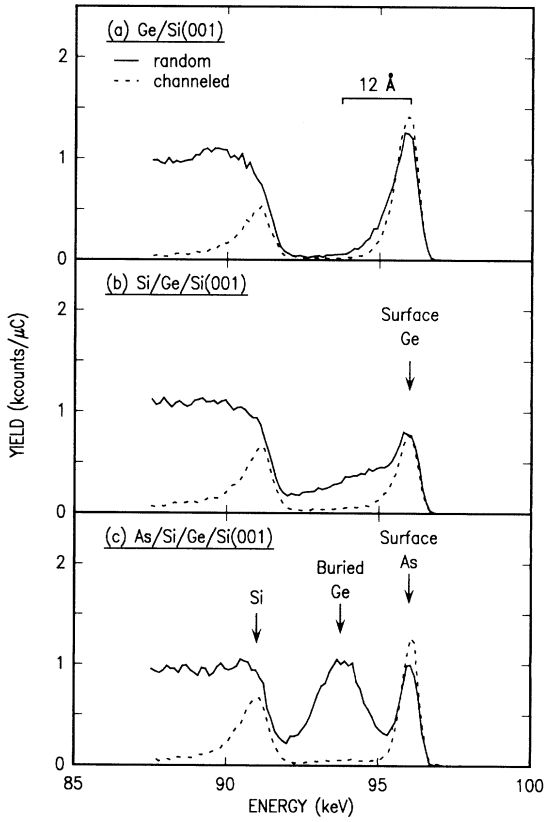

FIG. 2. Ion backscattering spectra for 1.5-ML GE films both with and without a Si cap. Both random and channeling geometries are shown. (a) Initial Ge overlayer without any Si cap. (b) Ge film after deposition of 8 ML of Si without an As passivation layer. Substantial amounts of surface Ge are still evident due to islanding of the Si cap. The tail on the Ge peak in the randomly incident spectrum is due to Ge buried by Si islands. (c) Ge film after a Si cap has been grown with an As passivation layer. All other growth conditions are identical to (b), but the Ge is not embedded.

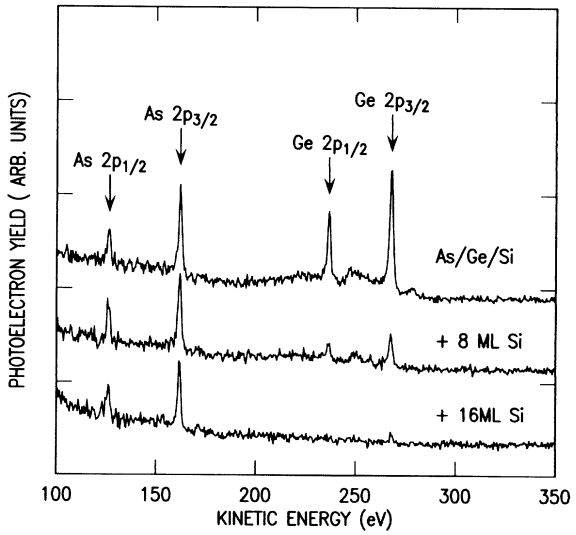

FIG. 3. Photoemission spectra for As-passivated films. Core lines are shown for films before and after deposition of a Si capping layer. While the Ge core lines decrease in intensity, the As core line remains approximately constant, indicating surface segregation of the As and embedding of the Ge.

Ge backscattering are indistinguishable due to the similarity in masses, we identify the higher-energy peak as backscattering from surface As. Below, we will confirm our identification using XPS. The random-incidence spectrum (solid curve) contains an additional peak due to the Ge layer, which is now embedded under the Si cap. The Ge peak is shifted to a lower energy due to energy loss of the backscattered ions in transversing the Si cap. The χ_{min} of the Ge film is indicative of epitaxial growth of both the Ge and the Si cap: χ_{min} is 5.8% for the embedded layer, while we find $\chi_{min}=5.1\%$ for Si at a similar depth in a virgin sample.

Further measurement by photoemission spectroscopy corroborates that the surface does indeed remain As terminated. Core-level spectra were taken using Al $K\alpha$ radiation and an emission angle of 45° (Fig. 3). The As and Ge $2p_{1/2}$ and $2p_{3/2}$ lines are included, as indicated in the figure. When 1.5 ML of Ge are deposited on an As-passivated Si(001) surface, the Ge and As core lines have an intensity ratio of 1.6. After deposition of Si at 470 °C, the Ge peak is attenuated by the Si overlayer, but the As line remains at nearly the same intensity. Spectra are shown for 8- and 16-ML Si overlayers. The continued presence of the As $2p_{1/2}$ and $2p_{3/2}$ core lines is evidence that the As layer floats to the surface during growth, confirming our interpretation of the MEIS data. Quantitative modeling of the attenuation of the Ge $2p_{3/2}$ core line using the data for an 8-ML Si cap results in a decay length of 14 Å, in reasonable agreement with the reported decay length of 10 Å.[15]

Growth of heteroepitaxial structures often involves a triumph of kinetics over energetics. For embedded films of electronically similar materials, it is inevitable that either the embedded heterolayer or the homoepitaxial capping layer has an unfavorable growth mode. The traditional method of overcoming this difficulty is to restrict the growth kinetics to inhibit islanding. This can be achieved either by decreasing the growth temperature or by increasing the growth rate. However, restricting growth kinetics also reduces the epitaxy of the film.

We have demonstrated an alternative approach to the dilemma, based on altering the energetics of growth by using a surfactant. Thus, island formation and interdiffusion are kinetically inhibited without any sacrifice of epitaxy. This approach need not be limited to Si-Ge, to As, nor to dopants in general. The primary requirements for the surfactant are that it reduces the surface free energies of both the substrate and the overlayer, and is sufficiently mobile to avoid incorporation. In other words, the surfactant must not preferentially adsorb to either substrate or overlayer, and it must surface segregate with high efficiency.

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