Influence of surfactants in Ge and Si epitaxy on Si(001)

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Epitaxial growth of heterolayers has in the past relied on optimization of growth conditions to overcome thermodynamic obstacles. When there is an intrinsic tendency of a heterolayer to either island or interdiffuse, a common strategy is to lower the growth temperature and increase the growth rate to reduce surface mobility. An alternative strategy is to introduce a surface-active species (surfactant) that modifies the growth mode without significant levels of incorporation. This paper discusses the application of As and Sb surfactants to the growth of Ge/Si(001) and Si/GeSi(001). Results from analysis by medium-energy ion scattering, x-ray photoemission, and ultraviolet photoemission are reported. By using a surfactant, island formation is suppressed in the growth of both Ge/Si(001) and Si/Ge/Si(001), resulting in thick, epitaxial films.

INTRODUCTION

Creating heterostructures is often an exercise in defeating the growth mode of an epitaxial layer. At sufficiently high temperatures to ensure epitaxy, the surface layer is, by necessity, quite mobile. This mobility allows the film to attain a thermodynamically stable structure, dictated by the combination of surface and interface free energies and the lattice strain of the heterolayer. For the case of Si and Ge, there is a small interface energy and limited intermixing, so the free energy will be minimized with a surface terminated by either the substrate species or the heterolayer. If one attempts to grow an overlayer that has a higher surface free energy than the underlying medium, the overlayer will island rather than wet the surface. In growing an embedded layer, first a heterolayer must be formed, followed by a capping layer of the substrate species. Only one of these two species can have the lowest surface free energy of the two. Thus, in growing an embedded layer, either the growth mode of the heterolayer, or the capping layer will be Volmer-Weber (i.e., immediate islanding). Furthermore, should there be significant lattice mismatch, island formation, strain-enhanced diffusion, and/or defects may arise after some critical thickness has been grown. For the Si/Ge system, the preferred surface termination is Ge, and the Ge lattice is 4% larger than the Si lattice, so that Ge will grow on Si(001) in the Stranski-Krastanov mode (layer-by-layer growth followed by islanding), while growth of Si on top of the Ge heterolayer follows the Volmer-Weber model.[1-3] Similar behavior is found for growth on (111) surfaces.[3-5]

We have explored the growth of films by molecular-beam eptiaxy (MBE) when the surface has been deliberately altered by a monolayer of As. The As acts as a surfactant, modifying the growth front by providing a stable termination of both the substrate and heterolayer that is energetically favored over either Ge or Si terminations. As a consequence, the morphology of the resulting film is dramatically affected, demonstrating the critical role of surface energetics in determining the growth mode of a film.

The microscopic structure of As on Ge(001) and Si(001) is well understood. Since As has one more valence electron than Ge or Si, a surface monolayer of dimerized As fills the otherwise dangling bonds of Ge(001) or Si(001), forming a (1×2) periodic array. Both photoemission results and theoretical analyses have supported this model.[6-8] Likewise, numerous investigations of As on Si(111) and Ge(111) have found a passivated (1×1) surface with the arsenic layer truncating a bulk-like structure.[9-11] A particular advantage to using As for a surfactant is that the coverage saturates at about 1 ML at 500 °C [1 monolayer $(ML) \equiv 6.78 \times 10^{14}$ cm^{-2}]. For a surfactant to function effectively, it must fulfill two criteria: it must be sufficiently mobile to avoid incorporation at a given growth rate, and it must surface segregate. Numerous dopants behave this way during epitaxy of group-IV materials. Indeed, we have achieved similar results for growth using As and Sb, suggesting that a variety of dopants can act as surfactants. A point that may be significant is that the As layer occupies epitaxial sites, possibly assisting any exchange mechanism with the incoming growth species.

In previous work we reported the fabrication of structures using surfactants, and outlined a mechanism for how surfactants affect growth.[12] Also, we examined with transmission electron microscopy (TEM) the microstructure of thick Ge films grown with a surfactant and described a newly observed defect that partially relieves the strain of the heterolayer.[13] In this paper, we will give a detailed analysis of how surfactants influence heterolayer morphology and composition, and discuss possible mechanisms for the formation of island-free epitaxial films. Providing that a saturation coverage of the surfactant is maintained, Ge films of unlimited thickness can be grown without islanding. The resulting film is not an alloy and contains dopant levels below our detection threshold.

EXPERIMENT

Si(001) samples were prepared by degassing at 600 °C for 12 h and light sputtering (500-eV Ar, 10^{14} ions/cm^2) to remove any surface carbon. The samples were then heated to 900 °C for a few minutes, followed by a 40 sec oxide flash-off at 1050 °C. Sample cleanliness was checked with x-ray photoemission spectroscopy (XPS) both after the initial cleaning, and during various stages of growth. It was found that the As capped surfaces show no carbon or oxygen buildup during growth. Samples were held at 500 °C during the depositions. Both Si and Ge growth rates were $\simeq 0.3$ ML/min. We were unable to directly measure the As flux, but the coverage saturated after 5–10 min, with the chamber pressure in the low-10^9-Torr regime, mostly due to arsenic. Si was evaporated from an electron beam heated crucible equipped with electrostatic plates to deflect Si ions from the sample. Ge was evaporated from a boron nitride crucible equipped with a quartz-crystal oscillator. Both the Sb and As sources were quartz effusion cells, with a quartz-crystal oscillation on the Sb cell.

The MBE system was attached to an ultrahigh vacuum medium-energy ion scattering (MEIS) system equipped with toroidal electrostatic ion optics to energy analyze the backscattered ions. Two different detectors were used to count the energy analyzed ions. The first detector consisted of an exit slit with channel plates and a one-dimensional position sensitive collector. In this configuration, ions over an angular spread of 20° scattering angle are detected simultaneously, but only one energy is measured at a time.[14,15] A second, newly developed detector was realized by removing the exit slit of the energy analyzer, decreasing the height of the sample spot from 0.5 to 0.1 mm, and replacing the one-dimensional collector with a two-dimensional collector.[16] In the new configuration, a spread of angles and energies are collected simultaneously, resulting in an improvement in both count rate and energy resolution. With the one-dimensional detector, an energy resolution of 500 eV is achieved for 100-keV ions, which is determined by the width of the exit spectrometer's exit slit and the sample spot size. However, the resolution of the two-dimensional detector relies principally on the spatial resolution of the collector, thus achieving an energy resolution of < 150 eV. Throughout this paper, we will follow the convention of plotting data from the one-dimensional collector as discrete points, while data from the two-dimensional collector will be plotted as a smooth curve. 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. Spectra are typically integrated over an angular range of $\pm 1°$ about the center of the detector, which was placed at a scattering angle of 54.74°, unless otherwise indicated. Coverages were measured by MEIS with an estimated accuracy of $\pm 5\%$. The thickest Ge films examined with MEIS (15 ML) showed a pronounced sensitivity to the ion beam, requiring doses below 10^{15} ions/cm^2 No such beam sensitivity was observed in the 1.5 ML films, suggesting that lattice strain may be responsible for the fragile nature of the thick Ge films.

Films were prepared by the following procedure: first, a clean Si(001) sample was dosed with a saturation coverage of As. Second, Ge was deposited with a continuous As flux to compensate for depletion of the surfactant. Although co-deposition was necessary to avoid islanding, XPS and MEIS observations, described below, eliminate the possibility of alloy formation. Upon completion of the Ge layer, the shutter was closed on the Ge cell, the Ge source was cooled, and the Si evaporator was warmed up, a process taking a few minutes. Finally, a Si capping layer was deposited, with the As flux turned off after the Si deposition had begun. In practice, it made no difference whether the As source was cooled before or after Si deposition began. For interrupted growth studies, the sample was left at the growth temperature, turned away from the MBE system, and a gate valve sealed off the sources from the sample. The system pressure immediately dropped to 10^{-11} Torr, and the sample was cooled. Since we found that no desorption of As took place during prolonged anneals at the growth temperature, the coverage measured closely resembles a snapshot of the system during growth.

GROWTH OF Ge/Si(001)

Backscattering spectra for Ge films (Fig. 1) embedded in Si(001) show a peak at 96 keV due to backscattering from surface As, and a peak at lower energies due to the buried Ge layer. The yield from the embedded Ge is well separated from the As, which resides on the surface. From a visual inspection of the spectra we can conclude two things about both the Ge and the Si growth: there are no islands, and the growth is epitaxial. If the Ge had, in fact, islanded, we would observe a saturation in the intensity at the Stranski-Krastanov thickness, but instead the Ge signal increases through 15 ML of growth. In addition, the Ge signal is shifted to lower energies than the surface As, indicating a continuous Si capping layer. Both channeling and random spectra are shown for each film, allowing us to assess the crystal quality of the film. For the As signal, the random and channeling spectra are practically identical, since there can be no shadowing of the surface layer of the sample. The Ge signal is greatly diminished in the channeling spectra, due to the presence of the overlying Si cap. Thus, we can conclude that both the Si and Ge are epitaxial, and that the As resides at the surface.

The ratio of channeled to random Ge yields, the so-called minimum yield (χ_{min}), was measured as a function of Ge coverage (Fig. 2). The data are compared to the work of Bevk et al., who have used conventional MBE to grow embedded Ge films.[17] In the samples examined by Bevk, a steep increase in χ_{min} occurs after 6 ML, indicating a breakdown in the film quality. Bevk et al. have exceeded the Stranski-Krastanov film thickness of 3 ML before the break in χ_{min}, possibly because the growth parameters allowed a larger, metastable film thickness. In contrast, the films grown using an As surfactant showed no sign of a catastrophic break in χ_{min} over the thicknesses examined. The low values of χ_{min} occur
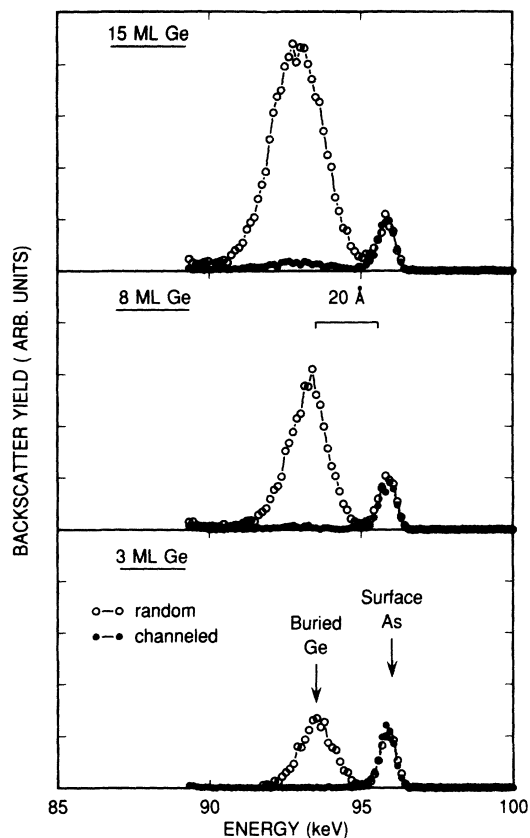
FIG. 1. Ion backscattering spectra for Ge films embedded in Si(001) using an As surfactant. The Ge film has been buried underneath a capping layer of 20 Å of Si, while the As has floated out with the growth front to reside on the surface. In the channeling spectra, the Ge is shadowed from the incident ions by the overlying Si, indicating that there is epitaxial growth of both the Ge and the Si.

FIG. 2. Minimum yield for Ge backscattering from embedded films. The data for films grown without a surfactant ($\blacktriangle$), taken from Ref. 17, shows a sharp increase in minimum yield with increasing Ge film thickness, due to a loss of epitaxy. But films grown with an As surfactant ($\bullet$) have only a very gradual increase in minimum yield.

despite the existence of strain relieving defects described in Ref. 13. Since the defects are built from microcrystals, which are expected to have a low dechanneling cross section, and are spaced $d \simeq 200$ Å apart, it is understandable that their presence has only a small effect on χ_{min}.

Due to the lattice mismatch between Si and Ge, it is energetically favorable for a germanium heterolayer to form unstrained islands. Examination of Ge films grown with As co-deposition show that strain is fully relieved without island formation after about 50 ML.[18] Once the strain is relieved, there is no longer a driving force for island formation, and the growth process is now similar to Ge homoepitaxy. It is therefore safe to assert that the film is of sufficient thickness to demonstrate that Ge heterolayers of unlimited thickness can be fabricated without islanding. Indeed at this point it is likely that the surfactant no longer serves an important role, and the As flux can be turned off, allowing the surface layer of As to deplete during growth.

Since the Ge films grown using a surfactant are fabricated in an As-rich environment, the amount of incorporation is of serious concern. To establish that the effect
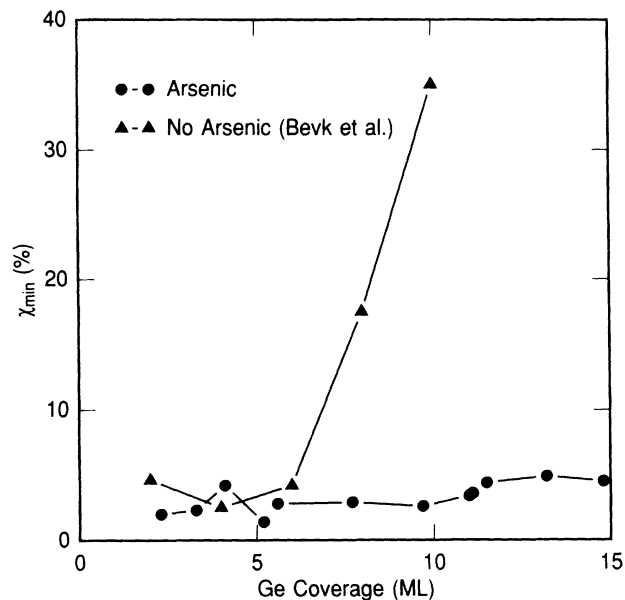
of the As on growth is indeed a surface phenomenon, as opposed to a bulk effect such as strain compensation, we have examined the films at various stages of growth using XPS and determined that the As content of the film is not sufficient to influence the structure. Photoelectrons were excited using Al $K\alpha$ radiation, and collected at an emission angle of 45° from the surface. As the film grows, the Ge $2p_{1/2}$ core line rapidly increases and saturates after $\simeq 15$ ML, while the Si $2p_{1/2}$ exponentially decays (Fig. 3). Both of these are compatible with layer-by-layer growth throughout the examined thickness of 40 ML. The absence of island formation was confirmed by cross section TEM. We have also plotted the intensities of two As features: the $2p_{3/2}$ core line, which has an escape depth of $\simeq 5$ Å, and the LMM Auger line (which is excited by the incident x rays), which has an escape depth of $\simeq 20$ Å. Neither line undergoes a significant change in intensity. If there was significant Ge-As alloying, we would expect to see an increase in the As LMM Auger, since it is a less surface sensitive feature. Placing an upper limit on the increase in the LMM intensity of 10%, we can limit the bulk concentration of As to $\lesssim 1\%$. Since the surfactant depletes during growth and it is not incorporated in the film, desorption must occur. Prolonged anneals without a Ge flux did not reduce the surface As concentration, implying that desorption is assisted by the Ge flux. The authors are unaware of any reference to MBE assisted desorption of surface species, a phenomenon that, if confirmed with further study, could prove important in modeling incorporation of species during growth.
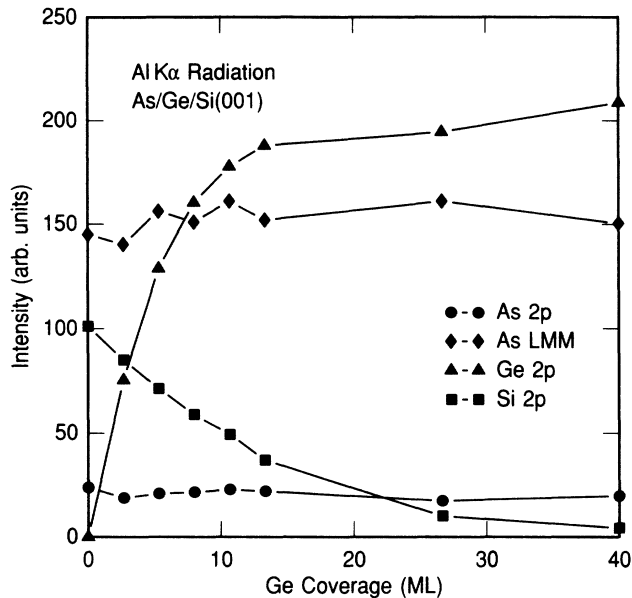
FIG. 3. X-ray photoemission intensities plotted for different Ge film thicknesses. With increasing film thickness, the Si $2p$ core line is attenuated, while the Ge $2p$ core line grows. Throughout the thicknesses examined, both the As $2p$ and the As *LMM* Auger lines remain uniform in intensity, indicating that both the surface and total film content of As are relatively constant.
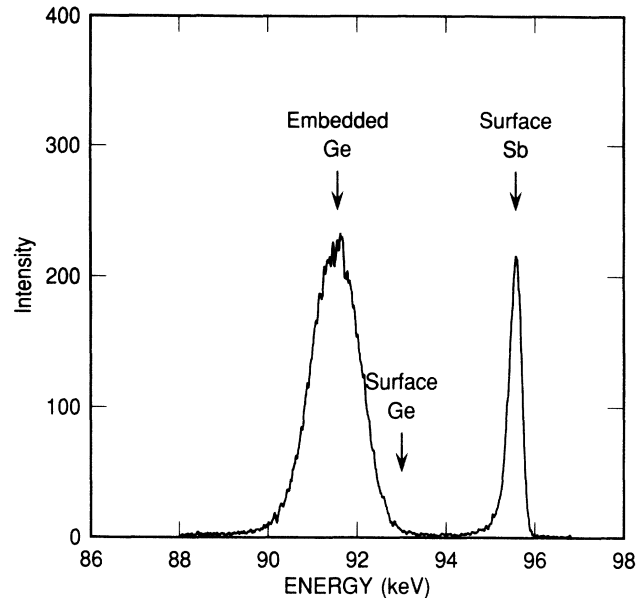
FIG. 4. Embedded Ge film grown with an Sb surfactant layer. The Sb backscatter signal, occurring at a 95.6 keV, is confined to a narrow surface peak with no bulk component. This indicates nearly complete segregation of the Sb during growth of both the Ge film and Si capping layer. A portion of the spectrum is shown for a scattering angle of 70.5°.

Further investigation of incorporation of the surfactant into the heterolayer dictated the use of a dopant with sufficient mass separation from Ge to allow us to resolve the two species by MEIS. Consequently, we replaced As with Sb and grew a 7 ML Ge film, capped with 12 ML of Si (Fig. 4). Saturation coverage of the Sb on the freshly grown surface varied from 0.7 to 0.9 ML, somewhat less than found for As coverage. Integration of the region behind the Sb surface peak results in a bulk concentration of $\lesssim 0.5\%$, indicating that the incorporation is below the measurement threshold for the techniques available in this study. Indeed, the actual dopant concentration could be far less than the range that can be detected with either XPS or MEIS. We note that the derived upper limit dopant concentration, 2.5×10^{21} cm^{-3}, is within the limits found by convention crystal-growth methods. Admittedly, the experimental probes available in the present investigation are not ideally suited to the task of measuring dopant incorporation levels, and such information is needed to evaluate the practicality of growing device quality material.

Although islanding was prevented in thin Ge films grown using Sb, the films were less stable than those grown using As. There are also significant differences between As and Sb chemisorbed surfaces which may make As a more suitable surfactant on Si(001). Unlike As, Sb/Si(001) forms a disordered layer with a blurry, indistinct low-energy-electron-diffraction pattern. Indeed, scanning tunneling microscope STM images of Sb/Si(001) show an atomically rough surface.[19] Detailed studies of

Sb interactions with Si(001) find that the sticking coefficient of Sb$_4$ is near unity below 0.7 ML, then drops precipitously at higher coverages.[20] Furthermore, a decrease in binding energy is found at coverages close to 1 ML. We may conclude that there is a strong repulsive interaction between surface Sb atoms, possibly leading to the disorder observed in STM. The origin of the strong repulsion may lie in the larger covalent radius of Sb compared to Si or As. Alternatively, the dominant effect may derive from differences in how the two dopants bond to Si(001). The Si core level undergoes a 0.45 eV chemical shift when chemisorbed with As, but there is a negligible chemical shift upon Sb adsorption.[19,21] The differences in photoemission results have been ascribed to the much larger electronegativity of As, resulting in a strong bonding of the surfactant. The result is that during growth with Sb, the coverage of the surface may not be complete, the energetics are doubtlessly different, and the surface stress is possibly weaker than is the case with As. Finally, since the surfactant does not occupy epitaxial sites, it may hinder the epitaxy of the film.

GROWTH OF Si/Ge/Si(001)

Next, we will discuss epitaxy of a Si capping layer on a thin Ge film on Si(001). In this case the Ge layer is sufficiently thin (1.5 ML), to significantly reduce the importance of lattice strain. Several points that require discussion are the growth mode of the Si, the quality of Si epitaxy in the presence of the surfactant, and the capabil-

ity of growing repeated iterations of embedded layers to produce a superlattice. The procedure used above was adapted to growing a double-well sample consisting of 1.5 ML or Ge, followed by 15 ML of Si, repeated a second time to create a total of 44 Å grown with a surfactant (Fig. 5). The As source was only used prior to each Ge deposition to establish a saturation layer of the surfactant. Backscattering spectra of the finished sample show two clearly resolved Ge layers, with no indication of island formation. In earlier work, MEIS results were used to demonstrate that without a surfactant, islanding of the capping layer occurred.[12] Samples produced using a high growth rate, 0.3 Å/sec, did not island, but showed pronounced mixing of Ge into the capping layer, penetrating as much as 60 Å.[22] In samples grown using a surfactant, it is clear that neither islanding nor severe interdiffusion take place. Furthermore, quantitative modeling of the spectrum shows that the broadening of the Ge backscatter yield is compatible with energy straggling of the ions. The smooth curve in Fig. 5 is a model spectrum using a sample structure with atomically abrupt interfaces. Peak widths are based on convolving the depth distribution with the known detector resolution (0.5 keV) and the energy straggling of the ions. An experimentally determined value of 0.22 keV^2/(10^{15} atoms/cm^2) was used for the energy straggling, based on measurements of films grown at room temperature. Within the experimental limits, there can only be very limited interdiffusion between the Si and Ge.

A key issue in any novel form of growth is the quality of the epitaxy. In addition to the channeling data presented above, cross-sectional transmission electron
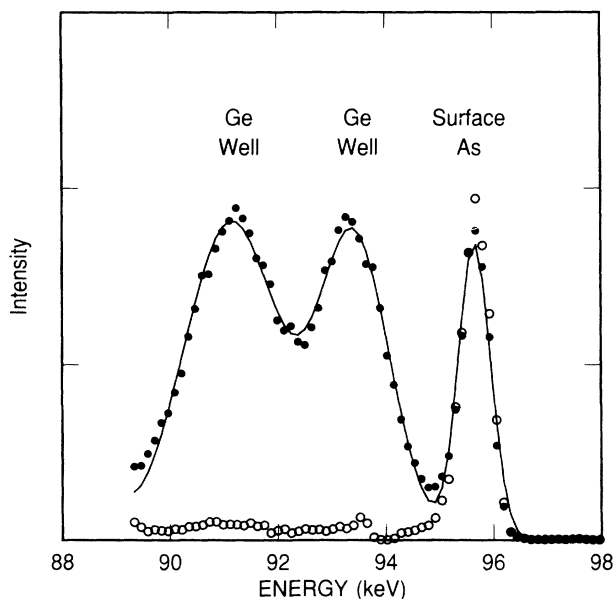

FIG. 5. Repeated iterations of As, Ge, and Si deposition were used to growth this double-well structure. Both channeling (○) and random (●) alignments are shown. The smooth curve is a model calculation assuming atomically abrupt interfaces as described in the text. The spectrum is shown for a scattering angle of 70.5°.

micrographs reveal that for thin Ge layers, where the strain is below the threshold for defect nucleation, there is epitaxial growth. From this we conclude that the presence of the surfactant does not interfere with the ability of the growth species to incorporate into epitaxial sites. We have proposed that a major effect of a surfactant is to alter the dynamics of the growth front. In the limit of a very short mean-free path for the incoming growth species on the surface, the incident atoms are incorporated at the nearest available lattice site. In this case, one would expect the growth front to roughen with film thickness, since the new atoms presumably arrive in a statistical distribution of lattice sites. But both the ion-scattering spectra and the cross-sectional TEM results indicate a well-defined Ge layer, suggesting that the mean-free path is sufficiently long for nearly layer-by-layer growth despite the presence of a surfactant. But the surface transport must be sufficiently inhibited to prevent island formation. Thus, we may think of the growth front in the following manner: the incoming species may travel some distance along the surface before being incorporated underneath the As layer. Once incorporated, the species are relatively immobile, subject only to bulk diffusion processes.

ELECTRONIC STRUCTURE

So far, we have investigated the structure of films grown with a surfactant, and ascertained that As does indeed float along with the growth front. But to complete the picture, we must examine the electronic structure during growth, since it is the electronic structure of the dopant that drives the surface segregation. We have used ultraviolet photoemission spectroscopy to look at the surface during various stages of growth. Spectra were taken using He I radiation at 21.2 eV, and photoelectrons were collected along the surface normal direction with a hemispherical energy analyzer. Photoelectron energies have been referenced to the top of the valence band (E_v) using the established separation between E_v and the Fermi energy of the clean Si(001) surface of 0.46 eV.[23] On the As terminated surfaces, the Fermi-level shift was measured by the change in the Si 2p peak binding energy.

First, let us examine the changes in electronic structure induced by chemisorption of As on the clean Si(001) surface (Fig. 6). On the clean surface, we observe a pronounced peak at 0.35 eV below E_v. This peak is due to electrons in the π bonding state associated with the dangling bonds on the Si dimers found on the reconstructed surface.[24] Upon exposure of the surface to As, the surface state is replaced by one 1.2 eV below E_v, caused by two different (nearly) degenerate surface states, the π bonding state and the π^* antibonding state.[6] By adsorbing a surface layer of As, and providing an extra valence electron, there are now two occupied dangling-bond states, compared to clean Si(001), where there is both an occupied and an unoccupied state. It is the presence of the occupied π and π^* states that provides the driving force for segregation of the surfactant during growth. Thus, by monitoring the electronic structure of the sur-
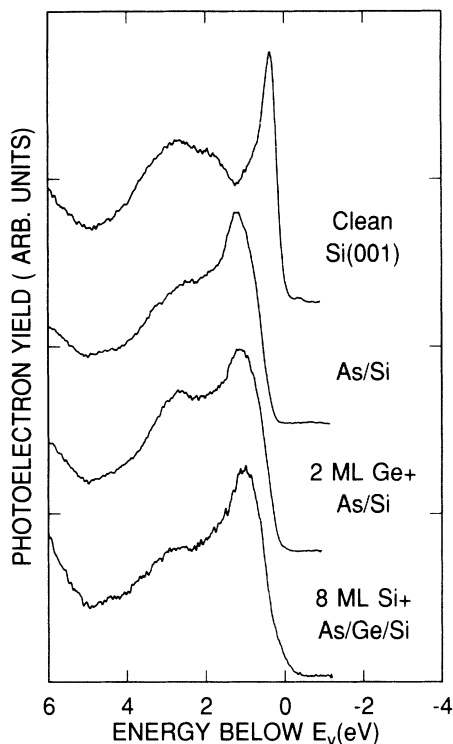
FIG. 6. Ultraviolet photoemission spectra of surfaces at various stages of growth. Before adsorption of As, there is a strong surface state at 0.35 eV below E_v due to unpaired dangling bonds. After adsorption of As, there is a surface state at 1.2 eV below E_v caused by the fully occupied dangling bonds of the As dimers. The state remains at all subsequent stages of growth.

face we can directly show that the π^* band remains occupied throughout all stages of growth, thereby demonstrating that the surface remains terminated by As dimers.

After depositing 2 ML of Ge on an As terminated Si(001) surface, the surface state remains unchanged, even though the As dimers now reside on a Ge layer (Fig. 6). Furthermore, after continuing to grow an 8 ML Si layer on top of the Ge, the photoelectron spectrum is nearly identical to that found for As/Si(001). If at some point the As were buried in a subsurface site, one would expect to see a return of the clean surface state at 0.35 eV below E_v. This demonstrates that throughout all stages of growth, As remains on the surface, continuing to passivate the surface dangling bonds.

MECHANISMS

Although we have presented extensive results on the effect of a surfactant on growth, the reason why this technique works is still uncertain. We can suggest two possible mechanisms, both of which may be operative. The first, proposed in earlier work, is a dynamic mechanism based on enhanced incorporation of the growth species. The second is a static mechanism based on the stress of a chemisorbed layer.

The effect of a surfactant on surface dynamics may be understood on an intuitive basis. Since dopants are energetically driven to surface segregate, during growth the surfactant will drive any incoming species to a subsurface site. Once the species is incorporated, the mobility is severely curtailed. Energy-minimization calculations based on norm-conserving pseudopotentials verify the strong tendency of As to segregate. A comparison of (001) slab energies for $\cdots$Si/Ge/Si/As and $\cdots$Si/Ge/As/Si show a difference of 2.3 eV per dimer favoring the segregation of As. Likewise, a comparison of $\cdots$Si/Ge/As and $\cdots$Si/As/Ge favors As termination by 1.4 eV per dimer. In view of such large energy differences, it is reasonable to suppose that site exchange between the surfactant and the Si or Ge takes places rapidly enough to alter the growth dynamics. In fact, there is a profound difference between the dynamics of growth with and without a surfactant. If we imagine an atom condensing from the vapor phase onto a clean surface, it must first exist as an isolated surface atom. The surface atom is free to migrate, until it reaches a step or some other defect site. There is, in fact, little to prevent the atom from moving. In the presence of a surfactant, there may be some period during which an adsorbed atom is quite mobile, but once the atom is underneath the As, the diffusion is strongly reduced. The incorporation into a subsurface site may not require the presence of a step or a defect, but only a site exchange with the As adlayer.

The second mechanism is based on calculations by Meade et al.,[25] showing the stress of clean and chemisorbed (111) Si and Ge surfaces. The results, summarized in Table I, indicate that both clean and Ge covered Si(111) surfaces involve significant components of compressive stress. On the other hand, As chemisorbed surfaces involve even more substantial tensile stress. The origin of the tensile stress is not lattice misfit, but the result of the bond-angle distortion. Experimental measurements of sample bending caused by film growth on Si(001) confirm the trends predicted by Meade et al., supporting the idea that an adsorbed layer of group-V atoms

TABLE I. Stress due to clean and adsorbed surfaces of group-IV semiconductors. Results for (111) surfaces are from theory (Ref. 25). Results for Si(001) are from experimental work, and represent values relative to the clean surface (Ref. 26).

Surface	Stress (ev/1×1)	Direction	Ref.
Si(111)	−0.54	compressive	25
Si(111)/Ge	−4.45	compressive	25
Si(111)/Ge	−1.12	compressive	25
Si(111)/As	2.27	tensile	25
Ge(111)	−0.73	compressive	25
Ge(111)/As	2.64	tensile	25
Si(100)/Ge[a]	−0.73	compressive	26
Si(100)/As[a]	1.3	tensile	26

[a]Experimental determinations relative to the clean surface value.

may compensate for the stress of a heavily compressed Ga film.[26] A shortcoming of this mechanism is that it does not predict a change in growth mode, only an increase in the thickness that can be achieved before islanding. Therefore, we suggest that both mechanisms may assist in surfactant based epitaxy. A good test of the importance of surface stress would be to grow in the presence of a group-III adlayer, where compressive stress is predicted for both the heterolayer and the surfactant.

SILICON-GERMANIUM ALLOYING

The conventional picture of Ge growth on Si(001) and Si(111) is that 3 ML of pure Ge grow in a layer-by-layer mode, followed by islanding. It is, however, extremely difficult to assess whether there is intermixing of Ge and Si before the Stranski-Krastanov thickness is grown. One way of evaluating the intermixing is by quantitatively analyzing the peak widths of the Ge backscatter signal. For the case of heavy intermixing, one would expect a significant broadening of the Ge peak. We have measured Ge peak shapes for room-temperature growth, where intermixing is expected to be quite limited, and for 500 °C growth. A visual inspection of the backscatter peaks (Fig. 7) reveals that for room-temperature growth, no significant broadening occurs, but for growth at

elevated temperatures, the Ge peak expands noticeably. The peaks were fitted using a Γ function, which has been previously used in fitting backscatter peaks for Ag/Si(111).[27] The Γ function is a curve defined by three independent fitting parameters: width, height, and asymmetry. The calculated peaks were convoluted with a detector resolution of 150 eV and the isotopic spread of Ge. An example of the Γ function before and after convolution is included in the bottom frame of Fig. 7.

The deconvolved Ge peak widths show no temperature dependence at low coverages, but a substantial broadening at the Stranski-Krastanov thickness (Fig. 8). The broadening cannot be solely due to film roughening effects, but the Ge must be diluted with another species with appreciable stopping power. Thus, we can conclude that the Ge is intermixing with Si for elevated growth temperatures. The uncertainty in stopping power precludes an exact determination of the extent of Ge-Si alloying, but an estimate based on the tabulated stopping powers places the composition at 20–40 at. % Si.

It is interesting to note that post growth annealing of the room-temperature film gave no discernible change in peak shape, suggesting that the intermixing takes place *during* growth. It is also important to realize that for the case of embedded layers, alloying is asymmetrical in the growth direction. Thus, for a superlattice, significantly more intermixing should be expected than is found in the present study. Also, it must be emphasized that the alloying we observe takes place *before* the Stranski-Krastanov layer is completed. At higher coverages, is-
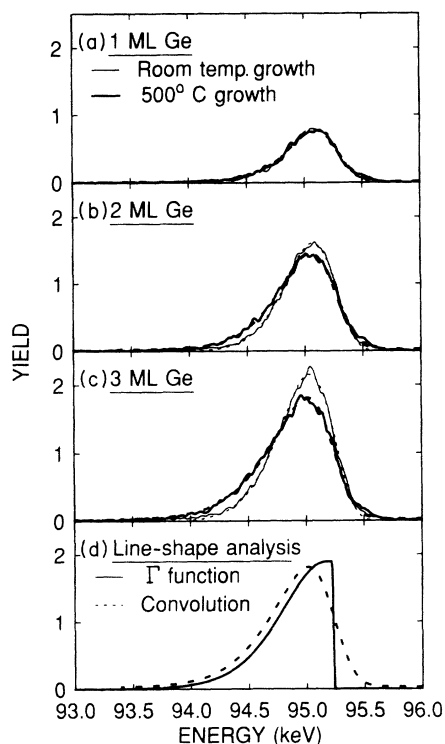

FIG. 7. Ge backscatter peaks for 1, 2, and 3 monolayer films on Si(001). Films were grown at room temperature (light curve) and 500 °C (bold curve). A distinct broadening can be seen in the 500 °C data, due to mixing of the Ge with the Si substrate. In the bottom frame the fitting function is plotted before and after convolution with the isotopic spread and the detector resolution.
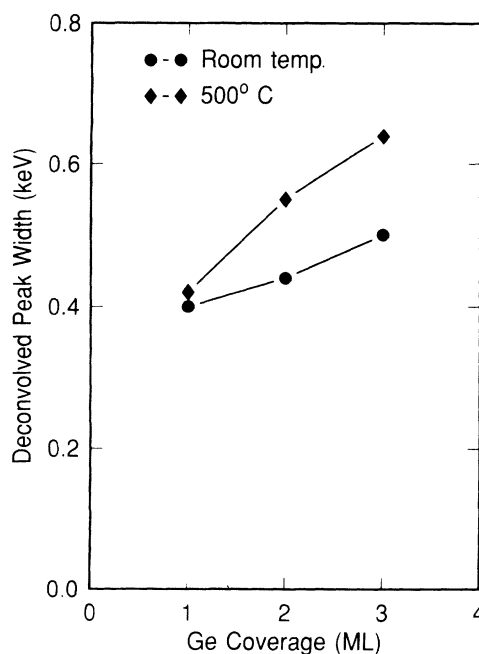

FIG. 8. Coverage dependence of the Ge peak width after deconvolution. Data is for samples grown at room temperature (●) and 500 °C ⟨◆⟩. At 3 monolayers coverage, there is a significant increase in the deconvolved peak width of the sample grown at 500 °C. The broadening is caused by the additional stopping power of Si that has alloyed with the Ge layer.

landing, and not indiffusion, is observed, although we have no means of establishing whether the islands are composed of pure Ge.

CONCLUSIONS

We have examined the effects of modifying epitaxial growth with a surfactant. A single atomic layer of a dopant is sufficient to alter the growth morphology of a group-IV heterolayer without alloying of the surfactant with the epilayer. The dopant is truly a surfactant, inducing films to grow in a continuous, layer-by-layer fashion solely by affecting the surface properties of the system, with no significant adulteration of the bulk. Using a surfactant, Ge heterolayers on Si(001) can be fabricating to unlimited thicknesses, demonstrating the conversion from a Stranski-Krastanov growth mode to a Frank–Van der Merwe growth mode. During the first 15 ML of growth, crucial to establishing the film microstructure, low-minimum yields are maintained, indicating

good crystal quality. In addition, TEM observations at a wide sampling of film thickness confirm that the film is both epitaxial and continuous. Fundamental understanding of how a surfactant works is still on somewhat uncertain grounds. Two possibly complimentary mechanisms have been proposed, both of which are compatible with the current understanding of dopant interactions with nonpolar semiconductor surfaces. Observation of the effect of a surfactant on long-range surface ordering during growth, either by scanning tunneling microscopy or by a diffractive probe such as electron diffraction, would be helpful in completing our understanding of how a surfactant works. Further work on the electrical properties of surfactant grown structures are essential to establishing the viability of this technique for device fabrication.

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[1]K. Sakamoto, T. Sakamoto, S. Nagao, G. Hashiguchi, K. Kuniyoshi, and Y. Bando, Jpn. J. Appl. Phys. 26, 666 (1987).

[2]M. Asai, H. Ueba, and C. Tatsuyama, J. Appl. Phys. 58, 2577 (1985).

[3]G. J. Fisanick, H. Gossmann, and P. Kuo, Epitaxy of Semiconductor Layered Structures, Vol. 102 of The Materials Research Society Symposium Proceedings, edited by R. T. Tung, L. R. Dawson, and R. L. Gunshor (MRS, Pittsburgh, 1987), p. 25.

[4]T. Narusawa and W. M. Gibson, Phys. Rev. Lett. 47, 1459 (1981).

[5]P. M. Marée, K. Nakagawa, F. M. Mulders, and J. F. van der Veen, Surf. Sci. 191, 305 (1987).

[6]R. I. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. 56, 520 (1986).

[7]R. D. Bringans, R. I. Uhrberg, M. A. Olmstead, and R. Z. Bachrach, Phys. Rev. B 34, 7447 (1986).

[8]J. F. Morar, U. O. Karlsson, R. I. Uhrberg, J. Kanski, P. O. Nilsson, and M. C. Qu, Appl. Surf. Sci. 41, 312 (1989).

[9]R. D. Bringans, R. I. Uhrberg, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. 55, 533 (1985).

[10]M. A. Olmstead, R. D. Bringans, R. I. Uhrberg, and R. Z. Bachrach, Phys. Rev. B 34, 6041 (1986).

[11]R. I. Uhrberg, R. D. Bringans, M. A. Olmstead, and R. Z. Bachrach, Phys. Rev. B 35, 3945 (1987).

[12]M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, Phys. Rev. Lett. 63, 632 (1989).

[13]F. K. LeGoues, M. Copel, and R. M. Tromp, Phys. Rev. Lett. 63, 1826 (1989).

[14]R. M. Tromp, H. H. Kersten, E. Granneman, F. W. Saris, R. J. Koudjis, and W. J. Kilsdonk, Nucl. Instrum. Methods B 4, 155 (1984).

[15]J. F. van der Veen, Surf. Sci. Rep. 5, 199 (1985).

[16]R. M. Tromp, M. Copel, M. Horn von Hoegen, and M. C. Reuter (unpublished).

[17]J. Bevk, J. P. Mannaerts, L. C. Feldman, B. A. Davidson, and A. Ourmazd, Appl. Phys. Lett. 49, 286 (1986).

[18]F. K. LeGoues, M. Copel, and R. M. Tromp, following paper, Phys. Rev. B 42, 11 690 (1990).

[19]D. H. Rich, F. M. Leibsle, A. Samsavar, E. S. Hirschorn, T. Miller, and T. Chiang, Phys. Rev. B 39, 12 758 (1989).

[20]S. A. Barnett, H. F. Winters, and J. E. Greene, Surf. Sci. 165, 303 (1986).

[21]R. D. Bringans, M. A. Olmstead, R. I. Uhrberg, and R. Z. Bachrach, Phys. Rev. B 36, 9596 (1987).

[22]S. S. Iyer, J. C. Tsang, M. W. Copel, P. R. Pukite, and R. M. Tromp, Appl. Phys. Lett. 54, 219 (1989).

[23]G. Hollinger and F. J. Himpsel, J. Vac. Sci. Technol. A 1, 640 (1983).

[24]J. Ihm, M. L. Cohen, and D. J. Chadi, Phys. Rev. B 24, 4592 (1980).

[25]R. D. Meade and D. Vanderbilt, Phys. Rev. Lett. 63, 1404 (1989).

[26]A. J. Schell-Sorokin and R. M. Tromp, Phys. Rev. Lett. 64, 1039 (1990).

[27]E. J. van Loenen, M. Iwami, R. M. Tromp, and J. F. van der Veen, Surf. Sci. 137, 1 (1984).