

Local Dimer Exchange in Surfactant-Mediated Epitaxial Growth

R. M. Tromp and M. C. Reuter

IBM Research Division, T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 30 September 1991)

While the effectiveness of surfactants in suppressing islanding in Si/Ge heteroepitaxial growth has been demonstrated in previous studies, the atomic scale growth processes have remained unknown. Here we present images of the growing Si(001)/Ge surface obtained with *in situ* low-energy electron microscopy. From our observations we conclude that surfactant-mediated growth of Ge on Si(001) proceeds by highly local Ge incorporation with minimum surface diffusion. We propose a new two-dimer correlated exchange mechanism to explain this unusual growth mode, as well as the absence of islanding at high Ge coverage.

PACS numbers: 61.14.Hg, 61.16.Di, 68.35.Bs, 68.55.Bd

Fabrication of many state-of-the-art electronic devices, both in elemental and compound semiconductors, requires heteroepitaxial growth of one material onto another. Efforts to grow such structures are frequently complicated by islanding of the growing material due to a mismatch in surface energies, bulk lattice constants, or both. It was shown recently that islanding in the Si/Ge system can be suppressed effectively by use of a surfactant monolayer adsorbed on the sample during growth [1]. Suitable surfactants such as As and Sb strongly reduce the surface free energy of both Si and Ge surfaces [2], and float at the surface during growth. As or Sb termination of the sample is energetically favorable, and the growing species (Si or Ge) will therefore be rapidly incorporated in a subsurface site, thus preventing islanding. Thus, while the thermodynamics of surfactant-controlled growth is clear, not much is known about the details of the growth process. For instance, one may envision growth to proceed by rapid diffusion to and incorporation at step edges, giving rise to a step-flow mechanism. Alternatively, incorporation may occur through a much more local mechanism on the terraces, unrelated to the presence of steps. In this case one would like to know how 2D island nucleation takes place, and what the minimum stable 2D island size is. In both cases, the distance over which Ge atoms may diffuse is of relevance. A clear understanding of these basic issues is required to further our knowledge of the role surfactants may play in epitaxial growth.

In this Letter we present the results of an *in situ* low-energy electron microscopy (LEEM) study of surfactant-mediated growth of Ge on Si(001). Somewhat surprisingly, we find that Ge incorporation on the As-covered surface occurs in a highly local process, without significant step flow, unlike growth on the bare Si(001) surface. While incorporation of a single dimer on an As-covered terrace is energetically not favorable, we propose a new two-dimer correlated exchange process which eliminates four dangling bonds, resulting in a minimum stable 2D island size of two dimers. This explains both the observed growth mode and the suppression of 3D islands at high coverage.

LEEM was developed only recently by Bauer and Teliaps [3,4]. In our microscope a 15-keV electron beam is focused in the back focal plane of a magnetic immersion-type objective lens, held at ground potential. Sample and electron source potentials differ by only a few volts, so that the electrons are decelerated to a few eV before they strike the sample. There they undergo low-energy electron diffraction (LEED), and are accelerated back into the objective lens, forming a focused LEED pattern in the back focal plane. A Gaussian image at magnification $20\times$ is formed at a distance of 30 cm. This image is further magnified onto a channel-plate intensified phosphor screen, to a final magnification of $10000\times$. As in transmission electron microscopy, one may select a given diffracted beam with an aperture for dark-field or bright-field imaging. In this study all images were formed using a $(\frac{1}{2}, 0)$ beam at 3.5-eV electron energy. The beam was incident at glancing angle, such that the $(\frac{1}{2}, 0)$ beam exited along the electron optical axis to optimize image resolution.

Si(001) samples (*n* type, 2 m Ω cm) were mounted in a Ta cap, at the end of an alumina tube isolating the sample potential (near 15 kV) from ground. A clean surface exhibiting the characteristic two-domain (2×1) LEED pattern was obtained by repeated heating to 1250°C by electron bombardment from behind. The sample was then cooled to 630°C to perform the growth experiments during observation. Ge was evaporated from a water-cooled boron nitride Knudsen cell and As₄ from a liquid-nitrogen-cooled quartz Knudsen cell.

Figure 1 shows experimental results obtained for Ge growth without an As monolayer. Image (a) is the clean starting surface. Alternating terraces, separated by single-height atomic steps exhibit (2×1) and (1×2) reconstructions, respectively. Since only the $(\frac{1}{2}, 0)$ beam was used for imaging, alternating terraces are black and white. The surface height increases from right to left. Images (b)-(d) were taken at increasing coverages. Growth of the first monolayer [1 monolayer (ML) = 6.78×10^{14} atoms/cm²] [image (b)] occurs by a step-flow mechanism; i.e., image (b) develops smoothly from image (a) by motion of the atomic steps, with full preser-

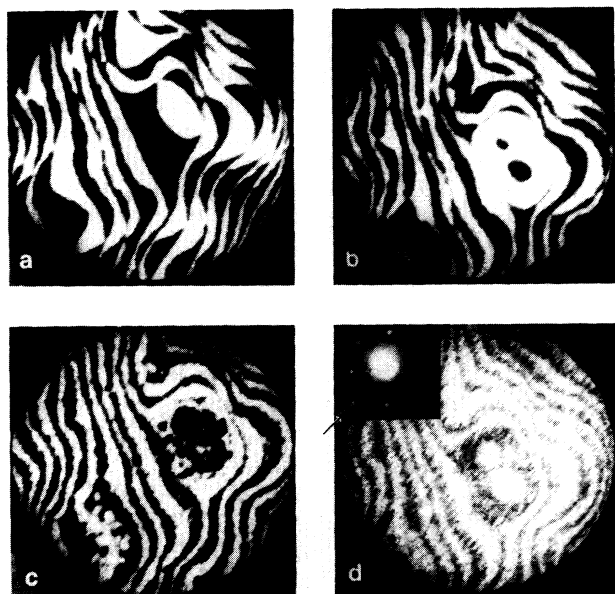


FIG. 1. LEEM images of Ge growth on clean Si(001). Approximate Ge coverages: (a) clean surface, (b) 1 ML, (c) 2 ML, and (d) 3 ML. Field of view is $4 \mu\text{m}$. The inset in (d) is a 5-eV LEED pattern taken on this surface at 3-ML coverage.

vation of the terrace contrast at all times. The second layer forms by nucleation and growth of 2D Ge islands [image (c)] on the larger terraces, combined with step flow. The third layer grows with much higher nucleation density of 2D islands over the entire surface [image (d)]. The image contrast disappears as the terrace sizes become smaller than the lateral resolution of the microscope (150 \AA). Continued growth leads to formation of 3D islands. The inset in (d) shows a 5-eV LEED pattern with bright (0,0) and half-order spots, as well as a broad, weak diffraction intensity in the $\langle 100 \rangle$ azimuths, resulting from surface roughening (see arrow). This roughening is driven by the 4.2% lattice mismatch between Si and Ge and allows for some strain relief in the overlayer.

Ge was grown on an As-terminated Si(001) surface by first saturating the surface with As to a coverage of 1 ML, followed by simultaneous exposure to Ge and As_4 fluxes [1]. Results are shown in Fig. 2. Image (a) shows the clean starting surface. Image (b) was taken after As adsorption to saturation coverage, but before Ge growth was started. One may notice that (b) is not simply the contrast-inverted equivalent of (a), as one would expect for adsorption of As dimers *on top* of the clean surface. This is due to displacement of Si surface atoms by As, even on the terraces far away from step edges. This phenomenon has been discussed before and will be further addressed in a separate publication [5]. Images (c)–(j) were taken at Ge coverages of about 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 ML. Immediately, the qualitative differences from the growth modes observed in Fig. 1 are obvious. In contrast to Fig. 1 step flow is never observed,

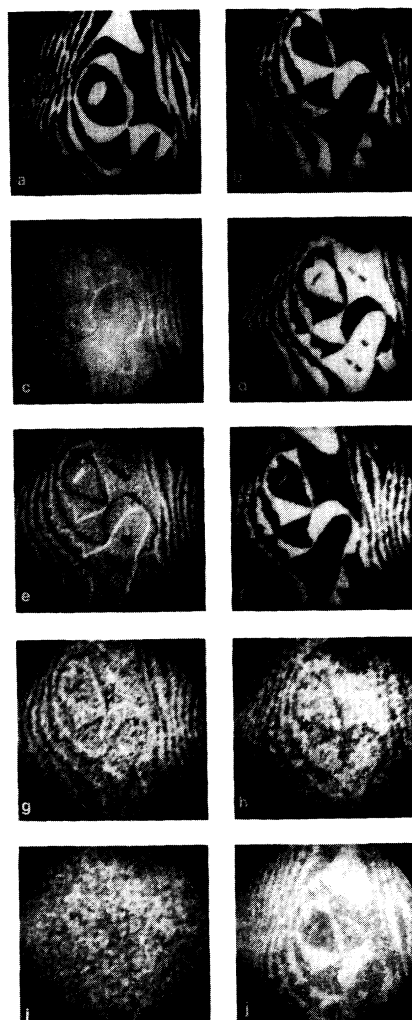


FIG. 2. LEEM images of Ge growth on As-terminated Si(001). (a) Clean surface and (b) As-terminated surface before Ge growth. Approximate Ge coverages: (c) 0.5 ML, (d) 1 ML, (e) 1.5 ML, (f) 2 ML, (g) 2.5 ML, (h) 3 ML, (i) 3.5 ML, and (j) 4 ML. Field of view is $4 \mu\text{m}$.

nor do we see nucleation and growth of relatively large 2D Ge islands at any Ge coverage. Instead, we see the contrast fade away at 0.5, 1.5, 2.5, and 3.5 ML, and reappear at 1, 2, 3, and 4 ML, although it gets weaker with increasing coverage. This alternation indicates that the growth mode is layer by layer, inverting the contrast with the completion of each ML of Ge by rotating the domain structure on a given terrace back and forth between (2×1) and (1×2) . The marked disappearance of contrast between full monolayers is indicative of nucleation of 2D Ge islands which are smaller than the resolution limit of the microscope. At half a monolayer coverage [image (c)] the surface is rough at a monolayer height level, with 2D island sizes smaller than 150 \AA , except near step edges where order is preserved somewhat better. The surface then becomes relatively smooth again

at 1 ML. This repeats for each additional monolayer, although residual roughness slowly builds up with increasing coverage. Beyond 4 ML the surface is permanently rough, and contrast is not recovered.

Thus, Ge adsorption without As shows step-flow growth, with 2D islands forming in the second and third layers to relieve some of the 4.2%-lattice-mismatch strain. Until the third layer is complete, the domain sizes are sufficiently large to be resolved. With As, however, 2D island formation starts immediately, with small, unresolved domain sizes. Apparently, the presence of an As monolayer provides a large driving force for the Ge atoms to incorporate in the surface very rapidly, with minimum surface diffusion. At first sight this may not seem surprising, since calculations show that the energy of Si(001)/Ge/As is lower than Si(001)/As/Ge by 1.7 eV per (2×1) unit cell [1]. That is, it is energetically favorable to terminate a full Ge layer with As. However, since growth does not proceed by instantaneous addition of full monolayers, the relevance of these calculations is questionable. To understand the incorporation of Ge dimers *during growth* we will consider Fig. 3 showing four rows of dimers (I, II, III, and IV). Row IV depicts the As-terminated starting surface. A Ge dimer can be adsorbed on top, as shown in structure (a). Structure (b) shows what we will refer to as "dimer exchange": Two Ge atoms have changed places with two As atoms. In both structures

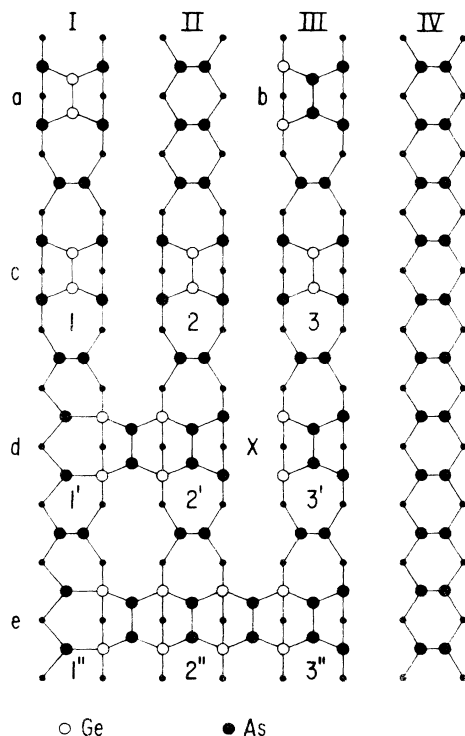


FIG. 3. Dimer exchange mechanism on As-terminated Si(001). For a full explanation see text.

(a) and (b) all As and Ge atoms are threefold coordinated, leaving a lone-pair orbital on the As atoms and a dangling-bond orbital on the Ge atoms. Since the number of dangling bonds remains constant upon single dimer exchange there is no clear energy benefit, and no strong driving force for subsurface incorporation of a single Ge dimer. However, the situation is very different for *two dimers*. Ge dimers 1 and 2 in structure (c) have a total of four dangling bonds, with all As atoms threefold coordinated. Now, let these two dimers simultaneously undergo a correlated exchange process, giving rise to 1' and 2' in structure (d). The four Ge atoms are now locally in the second layer, and fourfold coordinated. All As atoms are still threefold coordinated. Thus, the transition from (c) to (d) eliminates four broken bonds and is therefore energetically a highly favorable process that can occur locally, wherever two Ge dimers meet. Dimer 3' may also undergo dimer exchange (as shown). Adsorption of an additional Ge dimer at the position indicated by the cross, accompanied by dimer exchange, results in structure (e) and elimination of another four dangling bonds. Note that 2' and 3'' are identical and additional Ge dimer pairs can be appended in a similar fashion, giving rise to needlelike growth similar to that observed during low-temperature Si/Si(001) growth [6]. Indeed, we have observed such a growth mode in recent scanning tunneling microscopy experiments on this system [7]. Alternatively, additional dimer pairs may form new growth nuclei of type (c) elsewhere on the surface, as the two-dimer correlated exchange mechanism provides a favorable pathway for homogeneous nucleation of 2D islands.

1', 2', 1'', and 3'' are in effect single-height atomic steps (albeit only one dimer row wide). These steps are As terminated, not exposing any dangling bonds, and structurally similar to *B*-type steps observed on clean Si(001) [8].

We believe that the process described here explains the high nucleation density of 2D islands on the As-terminated growth system. It also explains why As is so effective in suppressing islanding. Without As, there is an equilibrium 2D vapor pressure of Ge dimers on the surface, continuously adsorbed and reemitted by the step edges. This equilibrium pressure of dimers on the terraces allows for nucleation of 3D islands when the critical thickness for island formation (3 ML) is exceeded, and also gives rise to Ostwald ripening of the islands [9]. When a dimer breaks away from a *B*-type step edge on the clean surface, there is no increase in the number of dangling bonds. The activation energy for this process is therefore low, and the free dimer concentration is relatively high. With As termination on the other hand there is a large driving force for dimer exchange, placing Ge atoms in subsurface sites. Ge dimers can only be formed in pairs [going from (d) to (c) in Fig. 3] at the expense of two broken bonds per dimer. The high activation energy for this process results in a low equilibrium concentration of free Ge dimers on the terraces, preventing nucleation

and growth of 3D Ge islands. Thus, while island formation may still be thermodynamically favorable (reducing mismatch strain energy), the process is strongly suppressed by the high activation energy for dimer emission from step edges.

In summary, we have presented the results of a LEEM study of growth of Ge on Si(001), with and without an As surfactant monolayer. We propose a new, two-dimer correlated exchange mechanism which explains both the observed growth mode at low coverage and the absence of Ge islanding at higher Ge coverage on the As-terminated surface.

The authors are indebted to Carlo Candotti, Frank Morgan, Earl Folsom, Charles Albert, and Richard Kaufman for their contributions to the design and construction of the microscope. It is also a pleasure to thank Dr. Joe Demuth and Dr. Andrew Zangwil for their stimulating interest in this work.

- [1] M. Copel, M. C. Reuter, E. Kaxiras, and R. M. Tromp, *Phys. Rev. Lett.* **63**, 632 (1989).
- [2] R. D. Bringans, R. I. G. Uhrberg, M. A. Olmstead, and R. Z. Bachrach, *Phys. Rev. B* **34**, 7447 (1986).
- [3] E. Bauer, *Ultramicroscopy* **17**, 51 (1985).
- [4] W. Telieps and E. Bauer, *Ultramicroscopy* **17**, 57 (1985).
- [5] P. R. Pukite and P. I. Cohen, *Appl. Phys. Lett.* **50**, 1739 (1987); T. R. Ohno and E. D. Williams, *Appl. Phys. Lett.* **55**, 2628 (1989); *J. Vac. Sci. Technol. B* **8**, 874 (1990); R. M. Tromp and M. C. Reuter (to be published).
- [6] R. J. Hamers, U. K. Koehler, and J. E. Demuth, *Ultramicroscopy* **31**, 10 (1989).
- [7] A. Denier van der Gon and R. M. Tromp (to be published).
- [8] R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).
- [9] M. Zinke-Allmang, L. C. Feldman, and S. Nakahara, *Appl. Phys. Lett.* **51**, 975 (1987).

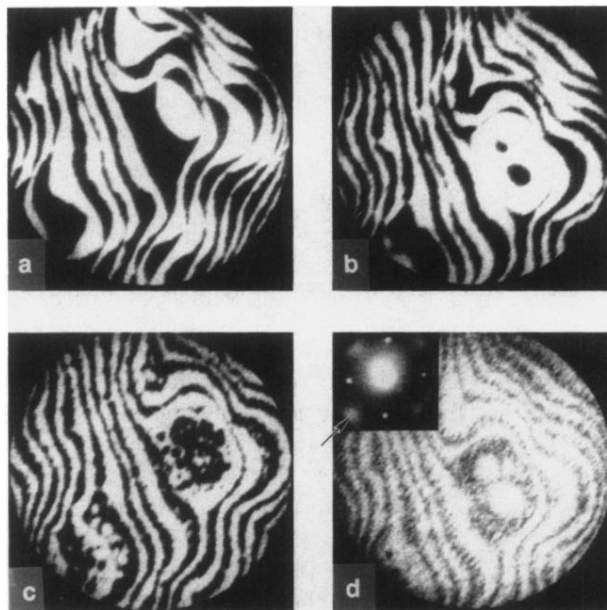


FIG. 1. LEEM images of Ge growth on clean Si(001). Approximate Ge coverages: (a) clean surface, (b) 1 ML, (c) 2 ML, and (d) 3 ML. Field of view is $4 \mu\text{m}$. The inset in (d) is a 5-eV LEED pattern taken on this surface at 3-ML coverage.

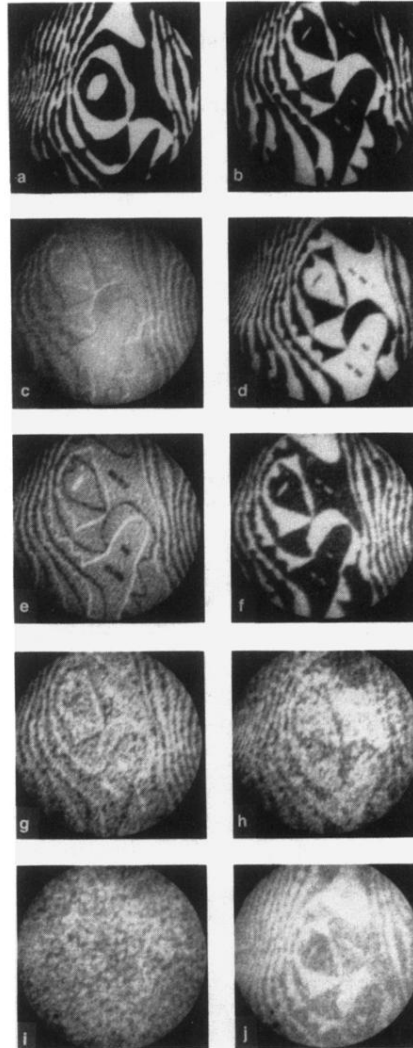


FIG. 2. LEEM images of Ge growth on As-terminated Si(001). (a) Clean surface and (b) As-terminated surface before Ge growth. Approximate Ge coverages: (c) 0.5 ML, (d) 1 ML, (e) 1.5 ML, (f) 2 ML, (g) 2.5 ML, (h) 3 ML, (i) 3.5 ML, and (j) 4 ML. Field of view is $4 \mu\text{m}$.