RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 11 15 APRIL 1991-I

Stress-induced layer-by-layer growth of Ge on Si(100)

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(Received 10 January 1991)

Several experiments have found that Ge initially grows layer by layer on the Si(100)2×1 surface, up to a thickness of 3 atomic layers. Further growth occurs via islands. Here, model calculations show that layer-by-layer growth is stabilized for up to 3 layers because it reduces the strain energy associated with the surface dimerization.

The growth of silicon, germanium, and their alloys from the vapor is surprisingly complex. Several fascinating issues have arisen recently involving steps and domains,[1,2] alloy ordering and surface segregation,[3–5] and island formation.[6–8] Intriguingly, all of these issues revolve around the role of surface stress and strain. Here we show that an outstanding puzzle in the growth of Ge on Si, the critical thickness of 3 Ge layers for the onset of island growth, is also attributable to the role of surface stress and strain.

Several experiments[6,7,9] have found that Ge grows layer by layer on the Si(100)2×1 surface, up to a thickness of 3 atomic layers. Further growth occurs via islands, which are initially coherent despite the 4% mismatch in lattice constants.[6,7] Such islands hinder the subsequent growth of sharp interfaces, e.g., for heterojunction devices or superlattices, so it is important to understand the forces which stabilize the desirable layer-by-layer growth for the first 3 layers.

The Ge islands which form after 3 layers exhibit interesting and unexpected behavior, such as coherent Stranski-Krastanow growth[6,7] and complex faceting.[10] However, here our concern is with the flat Ge film wetting the Si substrate between islands. We therefore consider the islands only as reservoirs of Ge, which determine the Ge chemical potential μ. Our goal, then, is to determine the equilibrium film thickness as a function of μ, and to identify the physical mechanism determining this thickness.

Some care is required in posing the problem of film thickness as one of equilibrium thermodynamics. In fact, the growth of Ge on Si is necessarily a nonequilibrium process, since in equilibrium on a substrate of pure Si, all the Ge would dissolve into the substrate. However, at typical growth temperatures of 500–700 °C bulk diffusion is negligible; so it seems reasonable to begin by ignoring intermixing between Ge film and Si substrate. This issue is discussed further below. There is still considerable surface diffusion above 500 °C, though, as indicated, e.g., by the motion of steps in response to stress.[11] Therefore, for sufficiently slow growth rates, an equilibrium will exist between the Ge film and the Ge islands, maintained by surface diffusion.

To determine the equilibrium film thickness, let U_n denote the energy per 1×1 cell of a Si(100) substrate plus n layers of Ge, terminated with the 2×1 dimer reconstruction. The energy required per atom to add an nth layer from a reservoir of Ge at chemical potential μ is $E_n - \mu$, where

$$E_n = U_n - U_{n-1} . \tag{1}$$

The system seeks to minimize its total energy including the reservoir, i.e., to minimize $U_n - n\mu$, so the condition for stability is that

$$E_n - \mu = 0 . \tag{2}$$

(Entropy plays little role here as discussed below.) If $E_n < \mu$, a film of $n-1$ layers will grow to n layers, while if $E_n > \mu$, a film of n layers will shrink to $n-1$ layers.

Figure 1 shows our central result, E_n vs n, for a modified Keating model.[12] The model and its motivation are described in detail below; but first we focus on the results, and their implications for film growth.

Given μ, the equilibrium number of layers of Ge for this model can be read directly from Fig. 1 according to Eq. (2), by noting where the layer energy E_n crosses the line $E_n = \mu$. So before going further, one must determine the appropriate range of μ. For large Ge islands whose strain is almost fully relieved by misfit dislocations, the chemical potential approaches that of bulk Ge, which we choose as our reference value $\mu = 0$. At the opposite extreme, if the

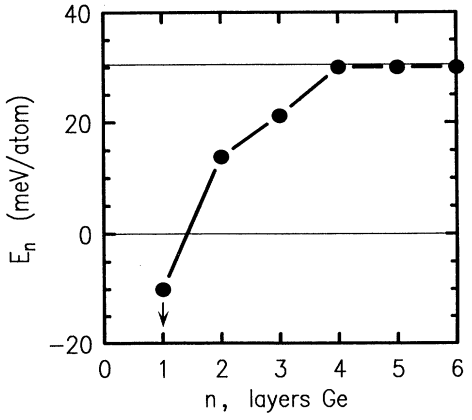

FIG. 1. Energy per atom E_n to add an nth layer of Ge on a Si(100) substrate, calculated with a modified Keating model. The arrow schematically suggests a lowering of the energy, for the first layer only, by effects neglected in this model, as discussed in text. Horizontal lines show the physically appropriate range of chemical potential.

islands are wide and fully coherent, then the chemical potential approaches that of bulk Ge biaxially strained to the Si lattice constant, around 30 meV/atom; but μ for the island is generally below this due to elastic relaxation of the island.[6,8] These bounds on μ are shown as horizontal lines in Fig. 1; the true value for a given surface in equilibrium should lie somewhere in between.

In the early stages of growth, where islands are coherent,[6,7] μ approaches the theoretical upper bound. Then from Fig. 1, three layers are expected. This is precisely the regime in which 3 layers of Ge have been observed experimentally.[6,7,9] Thus the results of Fig. 1 account for the central experimental observation; the underlying mechanism is discussed in detail below.

For late-stage growth, where islands are large and presumably nearly free of strain, μ should approach the lower bound. In that case, from Fig. 1 wetting by only a single layer of Ge is predicted in equilibrium. Such single-layer films have not to my knowledge been reported. This may be simply because the film thickness in this regime of high nominal coverage has not been studied. However, in addition it may be difficult to attain equilibrium in this regime except by halting growth and annealing.

During growth which is not sufficiently slow for full equilibrium, the surface may contain a mixture of islands of different degrees of strain. For still more rapid growth, a significant number of isolated atoms or clusters may be present, which could in effect drive up μ beyond the upper bound of Fig. 1 (to the extent that it is meaningful to speak of μ having a value at all in this case). This could lead to a film thicker than 3 layers, but in such a regime one cannot escape the necessity of considering kinetics explicitly.

For the entire relevant range of μ, one finds that the surface will be wetted by at least 1 layer of Ge. In fact, a surface dangling bond has lower energy cost for Ge than for Si, by perhaps 50 meV or more,[4] an effect neglected in the Keating model. So the first point in Fig. 1 should be displaced downward considerably, as suggested schematically by the arrow. Thus wetting is expected regardless of other details, simply because Ge has a much lower surface energy than Si. (The interface energy between Si and Ge is negligible on this scale.[4])

The energy differences between films of 1, 2, or 3 layers are of order 10 meV/atom, whereas at 600 °C the thermal energy kT is 75 meV. Nevertheless, there should be little thermal fluctuation in thickness. The film thickness cannot vary without forming steps, and these are of too high energy to be thermally generated except with large terraces. But for a large terrace, the differences in energy between 1, 2, and 3 layers will be correspondingly large, suppressing thermal fluctuations.

At this point, we have seen that calculated energies of Ge films can account for the experimentally observed film thickness. The physical origin of this multilayer wetting can be understood by noting that there are two primary differences between Ge and Si that are relevant here. First, Ge has a larger lattice constant, and second, it has softer elastic moduli. To separate the contributions of these effects, the calculation of Fig. 1 is repeated twice: once changing the substrate lattice constant to that of Ge, so that the only difference between film and substrate is the smaller elastic moduli of the film; and once changing the substrate elastic moduli to be close to those of the film, so that the only difference is the larger equilibrium lattice constant for the film. These two cases are shown in Fig. 2 as diamonds and squares, respectively. The sums of the respective values are shown as open circles. These are quite close to the original values of Fig. 1, shown as filled circles, confirming that the film's strain energy can be unambiguously decomposed into these two contributing factors.

The difference in elastic moduli favors wetting by 2 layers of Ge, as seen from the diamonds in Fig. 2. This is easily understood. Because of the dimer reconstruction, the Si(100) surface is under considerable atomic-scale strain, especially in the first 2 layers.[13] Thus one can save energy by substituting a softer material in those layers. Deeper in the bulk, the strain is small and little energy is gained by a thicker Ge film.

The difference in atomic size gives a somewhat more complex effect, as seen from the open squares in Fig. 2. The most notable aspect is that the second layer is made less favorable for Ge, consistent with earlier suggestions that the second layer is under local compression.[4] On the other hand, Ge in the third layer is slightly favored, making 3 rather than 2 layers of Ge the equilibrium thickness in the upper range of μ when both factors are included. For thick films, each additional layer merely adds a layer of bulk strained Ge.

The conclusion to be drawn is that the primary effect leading to a 3-layer Ge film is the energy gained by having a softer material in the near-surface region, where the strains associated with the reconstruction are large. However, the coupling of the Ge size difference to the surface stresses is also significant, and without this effect the Ge film would be only 2 layers thick.

Having explained the experimental results and inferred the physical mechanism at work, we now return to the de-

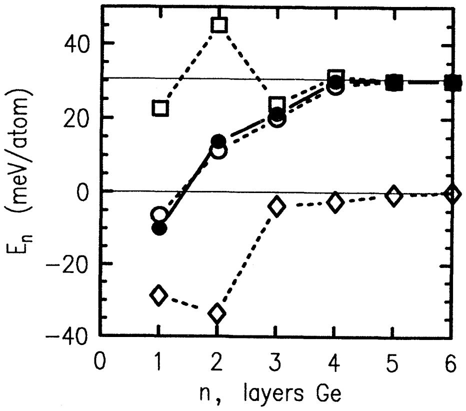

FIG. 2. Energy per atom E_n to add an nth layer of Ge on a Si(100) substrate, as in Fig. 1 (solid circles), plus the same calculation for two related models: where the substrate has its lattice constant modified to be the same as Ge (diamonds), or its elastic constants modified to be like Ge (squares). Open circles are sum of diamonds and squares for each n.

tails of the model. In the present model, the energy is

$$E=\sum_i \left[\sum_{j=1}^{4} \frac{\alpha_{ij}}{a_{ij}^2}(x_{ij}^2-\tfrac{3}{16}a_{ij}^2)^2 + \sum_{j,k>j}^{4} \frac{2\beta_i}{a_{ij}a_{ik}}(\mathbf{x}_{ij}\cdot\mathbf{x}_{ik}-\tfrac{3}{16}a_{ij}a_{ik}\cos\theta_i)^2 \right] . \quad (3)$$

Here $\mathbf{x}_{ij}$ is the vector connecting atoms i and j. Each pure material is described by three parameters: its lattice constant a_i, and its elastic parameters α_i and β_i. Thus these parameters take on only two values in Eq. (3), depending on whether atom i is Si or Ge. For bonds between Si and Ge, the parameters are assigned the geometric mean of their elemental values: $a_{ij}=(a_i a_j)^{1/2}$, and $\alpha_{ij}=(\alpha_i\alpha_j)^{1/2}$. For the pure materials this is simply the familiar Keating model[12] for the elastic energy, if we take all θ_i as the tetrahedral bond angle $\cos^{-1}(-\frac{1}{3})$.

For the present calculation, this potential is modified relative to the Keating model in the following way. Recognizing that there is some rehybridization for the threefold coordinated surface atoms, which can have an important effect on surface stress,[14] we allow θ_i to take on a different value for these atoms, denoted θ_s.

To determine the appropriate value of θ_s, the surface stress for Si(100)2×1 is calculated as a function of θ_s, and compared with parameter-free quantum-mechanical calculations of Payne *et al.*[15] and of Meade and Vanderbilt[16] using the local-density approximation (LDA) for correlation and exchange. The surface stress tensor is defined as

$$\sigma_{ij}^{\mathrm{surf}}=\frac{1}{A}\frac{dE^{\mathrm{surf}}}{d\varepsilon_{ij}} . \quad (4)$$

Here E^{surf} is the surface energy, A the surface area, and ε is the two-dimensional strain. Thus a positive value corresponds to tensile stress. Table I gives results for $\sigma_{\parallel}$ and $\sigma_{\perp}$, the stress components parallel and perpendicular to the surface dimers. The average stress $(\sigma_{\parallel}+\sigma_{\perp})/2$ is seen to be rather sensitive to the value of θ_s.

Physically, one expects that the threefold surface atoms will have a tendency towards sp^2 bonding,[14] favoring more open bond angles (i.e., a more negative value of $\cos\theta_s$) and hence a more compressive stress. This is consistent with the fact that an unmodified Keating potential ($\cos\theta_s=-\frac{1}{3}$) gives much too tensile a stress, compared with the LDA calculations.[15,16] In fact, the results of Payne *et al.*[15] are reproduced fairly well by the Keating model with $\cos\theta_s=-\frac{2}{3}$, while those of Meade and Vanderbilt[16] are similar to the Keating model with $\cos\theta_s=-\frac{1}{2}$. Thus either of these values seems more realistic than the unmodified Keating potential.

TABLE I. Calculated surface stress for Si(100)2×1 surface, in eV/(1×1 cell), parallel and perpendicular to the dimers ($\sigma_{\parallel}$ and $\sigma_{\perp}$), and their sum and difference, which measure the net tension and anisotropy. Results are for the modified Keating model (see text), with various values of the parameter θ_s, and for the LDA results of Refs. 15 and 16.

	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\sigma_{\parallel}+\sigma_{\perp}$	$\sigma_{\parallel}-\sigma_{\perp}$
Ref. 15	0.7	−2.0	−1.3	2.7
$\cos\theta_s=-2/3$	0.9	−2.1	−1.2	3.0
$\cos\theta_s=-1/2$	1.4	−1.0	0.4	2.4
$\cos\theta_s=-1/3$	1.7	0.1	1.8	1.6
Ref. 16	1.6	−0.9	0.7	2.5
$\cos\theta_s=-0.48$	1.5	−0.8	0.7	2.3

In Fig. 3, the calculation of Fig. 1 is repeated for these three values of θ_s. The results suggest that the stability of the 3-layer film is relatively insensitive to the choice of θ_s, except that for very large values of θ_s ($\cos\theta_s \lesssim -\frac{2}{3}$) only a 1-layer film is stable. This is easily understood in terms of the results of Fig. 2 and of Table I. Large values of θ_s lead to a more compressive stress. This in turn exacerbates the compression in the second layer, making it more unfavorable for Ge. When this penalty outweighs the gain from having additional layers with softer elastic moduli, there is no energy lowering from film thickening beyond 1 layer. (This interpretation has been explicitly verified by repeating the calculation of Fig. 2 with $\cos\theta_s=-\frac{2}{3}$.)

Since the results depend somewhat on θ_s, it seemed reasonable to choose this parameter to fit the LDA calculations. We chose[17] to fit the result of Meade and Vanderbilt, giving a value of $\cos\theta_s=-0.48$. However, as seen from Fig. 3, our conclusions remain valid for essentially all reasonable values of θ_s, except at the extreme of large compressive surface stress.

Finally, the problem of intermixing of the film and substrate deserves more detailed consideration than we can give it here. There is a considerable driving force for interdiffusion, beyond the usual entropic considerations. First, intermixing lowers the strain energy. Second, in an alloy additional energy can be gained by arranging the Si and Ge so as to compensate for the stresses associated with the surface reconstruction. This effect can be rather large on the present energy scale, of order 30 meV/atom even in the fourth layer.[4] Thus any intermixing will considerably complicate the problem by allowing such effects to come into play. However, such intermixing is necessarily kinetically determined, and so is beyond the scope

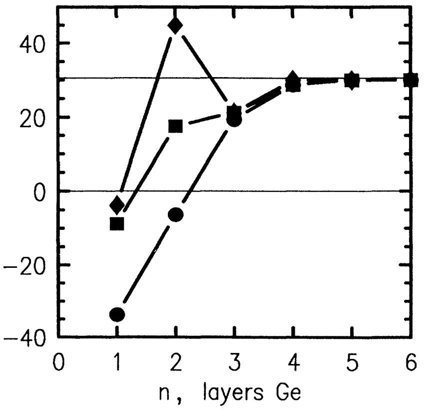

FIG. 3. Energy per atom E_n to add an nth layer of Ge on a Si(100) substrate, as in Fig. 1, but for three different values of the parameter θ_s: $\cos\theta_s=-\frac{1}{3}$ (circles), $\cos\theta_s=-\frac{1}{2}$ (squares), and $\cos\theta_s=-\frac{2}{3}$ (diamonds).

of our quasiequilibrium analysis.

Experimentally, Copel *et al.*[18] have observed that some intermixing occurs when Ge is deposited at 500 °C, but that intermixing is suppressed when the film is deposited at room temperature, even when subsequently annealed at 500 °C. This is consistent with the idea that there is considerable surface diffusion, but not bulk diffusion, at this temperature, since during growth intermixing can occur by what is essentially surface diffusion.

In conclusion, the energies of thin Ge films on Si(100)2×1 are reduced, relative to Si(100) plus biaxially strained bulk Ge, by having the strain from the surface dimerization fall in a material of smaller elastic moduli. In addition, the local stresses associated with surface dimerization favor having the larger Ge atoms in the third layer. The net result accounts for the observed 3-layer Ge film thickness in the initial stages of epitaxial growth. The results also predict that in true equilibrium between islands and film, when the islands become large and their strain is relieved by dislocations, the Ge film should shrink to a single atomic layer.

This work was supported in part by ONR Contract No. N00014-84-C-0396. Discussions with D. P. DiVincenzo and R. M. Tromp are gratefully acknowledged.

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