

Competing Relaxation Mechanisms in Strained Layers

J. Tersoff and F. K. LeGoues

IBM Research Division, Thomas J. Watson, Research Center, Yorktown Heights, New York 10598

(Received 12 January 1994)

We show that strained epitaxial layers can relax by two competing mechanisms. At large misfit, the surface becomes rough, allowing easy nucleation of dislocations. However, strain-induced surface roughening is thermally activated, and the energy barrier increases very rapidly with decreasing misfit ϵ . Thus below some misfit ϵ_c , the strain relaxes by nucleation of dislocations at existing sources before the surface has time to roughen. Relaxation via surface roughening is technologically undesirable; we discuss how temperature, surfactants, or compositional grading change ϵ_c and so control the mode of relaxation.

PACS numbers: 68.35.Fx, 68.55.-a

The relaxation of strain in epitaxial layers is a classic problem in materials physics, which has gained urgency with the growing application of strained layers in microelectronics. The classic work of van der Merwe [1] and of Matthews and Blakeslee [2] focused on the critical thickness to form dislocations *in equilibrium* in a uniform strained layer. However, recently there has been a growing recognition that in practice, strain relaxation is kinetically limited.

In many cases, the rate-limiting step in relaxation is presumed to be the nucleation of dislocations. Homogeneous nucleation cannot occur on laboratory time scales for strains of practical interest ($\lesssim 4\%$) [3-6]; but nucleation may occur at defects [6-8], or by "multiplication" of preexisting dislocation [8-10].

However, another possibility arises from the fact that uniform strained layers are unstable against modulation of the surface profile [11-16]. For convenience we refer to such strain-induced modulation generically as "roughening" (not to be confused with thermal roughening). The driving force for roughening is that, although it increases the surface area, it also allows a partial relaxation of the strain by purely elastic deformation of the film and substrate. Yang and Srolovitz [11] have shown that this roughening can take the form of sharp grooves or pits in the surface. These provide points of large stress where the barrier to nucleation of dislocations is extremely small, as has been emphasized by Jesson *et al.* [17].

Here we show that under reasonable assumptions, surface roughening is thermally activated, with a barrier which scales with misfit ϵ as ϵ^{-4} . In contrast, other mechanisms of dislocation nucleation typically give an ϵ^{-1} dependence for the barrier. Thus nucleation of dislocations via surface roughening should be kinetically favored at large misfit, while at smaller misfit, other mechanisms such as multiplication should dominate.

This prediction is confirmed by transmission electron microscope (TEM) studies of SiGe alloy layers grown on Si. We find that films with misfit $\epsilon < 0.01$ relax by a modified Frank-Read (MFR) multiplication mechanism [8], and the surface remains smooth throughout growth

and relaxation. Films with misfit $\epsilon > 0.012$ first become rough and then relax; and in this case relaxation is not by MFR. We infer that the large-misfit samples are relaxing by nucleation of dislocations at surface roughness.

Since surface roughness can lead to large local stresses and hence virtually barrierless nucleation of dislocations [11,17], we shall assume that the roughening process is the rate-limiting step in this mode of relaxation. Previous treatments [11-15] of strain-induced roughening have considered an isotropic continuum model. In that model, there is no barrier to surface roughening. However, real crystals are generally faceted in equilibrium, except at high temperature [18]. Faceting could in principle be destroyed if growth conditions are far from equilibrium [19]. However, studies of Ge and SiGe alloys grown on Si(100) [15,20] have generally indicated faceting. Moreover, the faceted morphology of our samples is somewhat visible in Fig. 4(c), and has been directly confirmed by atomic force microscopy [21].

We therefore assume that the surface can have only discrete orientations, so islands or pits have the shape shown in Fig. 1. More generally there could be multiple allowed orientations [21], with roughening proceeding through a sequence of progressively steeper facet angles, in analogy with the isotropic case. In that case we assume the formation of the first, shallowest pits to be the rate-limiting step, so that only one angle need be considered.

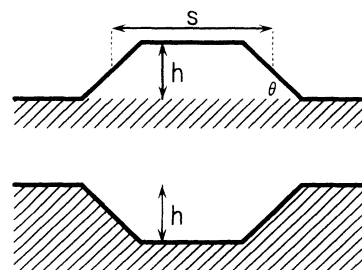


FIG. 1. Cross section of shape assumed for island or pit. Length and height are denoted by s and h . Edges are oriented at an angle θ with respect to the surface.

By simple geometry, the change in surface free energy to form either an island or pit as in Fig. 1 is

$$E_s = 2\Gamma h(s+t), \quad (1)$$

where $\Gamma = \gamma_e \csc\theta - \gamma_s \cot\theta$, and γ_s and γ_e are the surface free energy per unit area for the normal orientation and for the beveled edge, respectively. We neglect terms associated with the corners. The parameters s , t , h , and θ are the length, width, height, and contact angle, as in Fig. 1.

The reduction of the strain energy by elastic relaxation is more complicated, and in general must be treated numerically [11,13,16]. However, if we assume that the island or pit is rather flat ($h \ll s$), then one can approximate the relaxation energy [22] as

$$E_r = -\frac{\sigma^2}{2} \int d\mathbf{x} d\mathbf{x}' \chi_{ij}(\mathbf{x} - \mathbf{x}') \partial_i h(\mathbf{x}) \partial_j h(\mathbf{x}'). \quad (2)$$

Here \mathbf{x} and \mathbf{x}' are two-dimensional vectors on the surface, $h(\mathbf{x})$ is the height of the island or pit at position \mathbf{x} , and σ is the xx or yy component of the bulk stress of the uniform epilayer. The thickness gradient $\partial_j h(\mathbf{x})$ exerts a force density $f_j = \sigma \partial_j h(\mathbf{x})$ at point \mathbf{x} , causing a displacement $\chi_{ij}(\mathbf{x} - \mathbf{x}') f_j$ at \mathbf{x}' . (This relationship between force and displacement defines the surface Green's function χ .) Equation (2) then simply represents the work done in relaxing. Even when the island is too thick for Eq. (2) to be accurate, it should capture the important qualitative physics, which is all we require here.

Solving Eq. (2) using χ of an isotropic solid, and with some additional approximations [22,23], gives

$$E_r = -2ch^2 \left[s \ln \left(\frac{te^{3/2}}{h \cot\theta} \right) + t \ln \left(\frac{se^{3/2}}{h \cot\theta} \right) \right]. \quad (3)$$

Here $c = \sigma^2(1-\nu)/2\pi\mu$, and ν and μ are the Poisson ratio and shear modulus of the substrate. While an island and a pit are equivalent in this approximation, inclusion of higher-order terms always favors a pit [16], as long as the pit does not penetrate beyond the strained layer. However, if nucleation occurs before the film is thick enough to support pits, islands will form instead.

Minimizing the total free energy $E = E_s + E_r$ with respect to shape for fixed volume gives $s = t = h \cot\theta$ (s and t cannot be less than $h \cos\theta$). Then the volume is

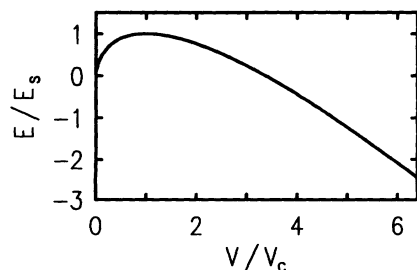


FIG. 2. Energy of island or pit, Eq. (4), versus volume. V_c and E_s are defined by Eqs. (5) and (6).

$V = h^3 \cot^2\theta$ [23], and the energy is

$$E = 4\Gamma V^{2/3} \tan^{1/3}\theta - 6cV \tan\theta. \quad (4)$$

The energy is shown versus volume in Fig. 2. Clearly formation of an island or pit lowers the energy once the structure is sufficiently large. However, there is a barrier E_s which must first be overcome.

Finding the maximum of Eq. (4), this barrier occurs at a critical size

$$V_c = (4\Gamma/9c)^3 \cot^2\theta, \quad (5)$$

and has height

$$E_s = 3^{-1} (4\Gamma)^3 (9c)^{-2} \cot\theta = U_s \varepsilon^{-4}. \quad (6)$$

Note in particular that the barrier scales with misfit as ε^{-4} (since $c \propto \sigma^2 \propto \varepsilon^2$), as we have emphasized by grouping all other parameters together into the term U_s .

Because of the energy barrier E_s , we expect the rate R_s of surface nucleation of pits (and hence of dislocations) to be $R_s \propto D e^{-E_s/kT}$, where D is the surface diffusion constant. At sufficiently high flux, this could be modified by kinetic effects (adatom supersaturation) during growth; but we shall confine ourselves to the regime of relatively slow growth. Then from Eq. (6), the nucleation rate is

$$R_s \propto D e^{-U_s \varepsilon^{-4}/kT}. \quad (7)$$

In contrast, the rate for homogeneous bulk or smooth-surface nucleation of dislocations can be approximated [3,24] as

$$R_b \propto e^{-U_b \varepsilon^{-1}/kT}. \quad (8)$$

Apparently MFR nucleation (and perhaps other inhomogeneous mechanisms as well) can also be approximated by Eq. (8) [24].

These two rates have very different dependences on misfit, as shown in Fig. 3. Clearly at small misfit the bulk nucleation mechanism dominates. Thus strain is relaxed by nucleation of dislocations *before* the surface has time to roughen. The driving force for roughening is then removed, so the film remains smooth at all times. This is the situation desired in most applications.

However, at some misfit ε_c the two rates are equal, and at larger misfit the surface will roughen *before* any dislocations are introduced. The roughness then provides a low-barrier path for formation of dislocations [17]. Once the strain is relieved by dislocations, the surface should gradually become smoother to lower its surface energy, but we are not concerned with such long-time behavior here.

We have observed precisely this behavior in SiGe alloy films grown on Si(001). Figure 4 shows films of compositions $\text{Si}_{1-x}\text{Ge}_x$ with $x=0.15$ and $x=0.30$ (misfits $\varepsilon=0.006$ and 0.012 , respectively). The films were grown by ultrahigh vacuum chemical vapor deposition at 560°C [8]. The low misfit sample is smooth before relaxation [Fig. 4(a)], and remains smooth after dislocations are introduced [Fig. 4(b)]. Other studies [25] have confirmed

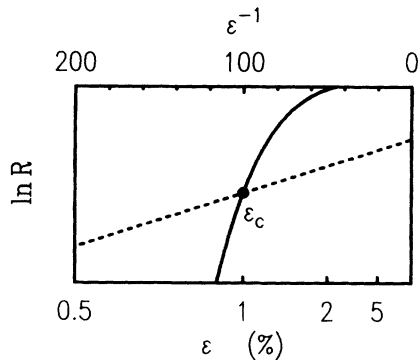


FIG. 3. Rate of introduction of dislocations by two competing mechanisms versus misfit ϵ . Dotted line is Eq. (8), characteristic of homogeneous nucleation. Solid line is Eq. (7), the rate of nucleation of pits, each of which provides a source for low-barrier nucleation of dislocations. Vertical scales of curves depend on the respective material-dependent parameters U_b and U_s , and the vertical origins depend on the respective prefactors. Dot indicates crossover between mechanisms at misfit ϵ_c .

that the film remains smooth throughout the relaxation process. It relaxes by the MFR mechanism [8], which can be recognized by the injection of dislocation loops deep into the substrate [see arrow in Fig. 4(b)].

In contrast, in Fig. 4(c) the high misfit sample is seen to roughen even before reaching the equilibrium critical thickness for the introduction of dislocations. After the film grows thicker and dislocations are introduced [Fig. 4(d)], the roughness is still evident. No dislocation loops are seen in the Si substrate in this case, confirming that relaxation is by a mechanism other than MFR. Previous experiments have also indicated a transition between two relaxation mechanisms as misfit is varied [24], although the mechanism at high misfit was not identified.

Our theoretical analysis should apply to any strained system, not just SiGe. And indeed, InGaAs grown on GaAs exhibits a similar transition in the mode of relaxation as a function of misfit [26]. Thus our results have broad implications for epitaxial growth of III-V and II-VI strained layers, as well as for SiGe.

We emphasize that surface roughness is highly undesirable in most application. It precludes subsequent growth of ideal planar interfaces. Moreover, it leads to high densities of threading dislocations, by creating a high density of sites where the barrier to dislocation nucleation is small. Thus methods of controlling the mode of relaxation are of considerable importance.

We can now understand more clearly how these methods work. The barrier E_s depends almost as sensitively on Γ as on the misfit ϵ , so modifying Γ is a powerful technique. If a surfactant increases Γ (e.g., by decreasing γ_s more than γ_e [27]), then it will tend to increase ϵ_c and so suppress roughening. [The surfactant may additionally inhibit surface diffusion, reducing the prefactors in Eq. (7).] We believe this explains the unusual relaxation of Ge on Si(100), when As is present as a surfactant. In

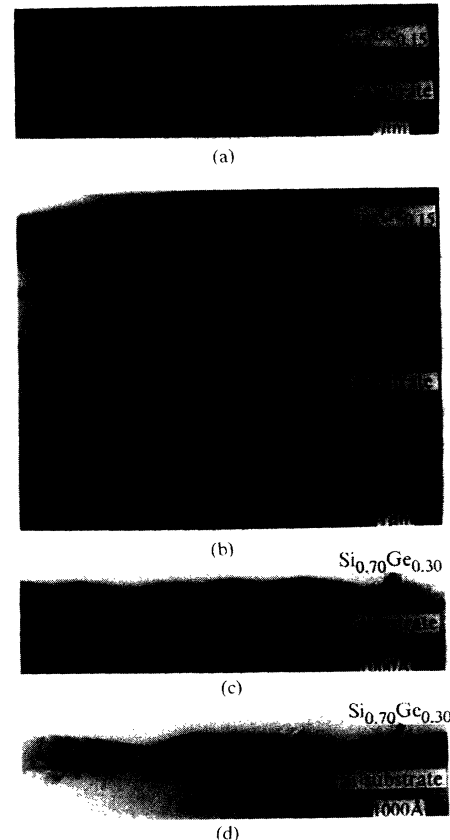


FIG. 4. Cross-sectional TEM images of $\text{Si}_{1-x}\text{Ge}_x$ films grown at 560°C on Si(100), as described in text. Note different scales. (a) 5000 Å layer at 15% Ge. The surface is flat, and no dislocations have formed. (b) 6500 Å layer at 15% Ge. The surface is flat, and dislocations have been introduced by the MFR mechanism, as evidenced by the pileup of dislocations deep in the Si substrate. Arrow indicates one dislocation in the pileup. (c) 200 Å layer at 30% Ge. The surface is rough, and no dislocations have formed. (d) 500 Å layer at 30% Ge. The surface is rough, and the sample has relaxed. Arrow indicates one of the threading dislocations visible in the film.

that case the film remains smooth; and relaxation occurs much later than without the surfactant, via formation of "V-shaped defects" rather than by roughening [28].

Elevated temperature reduces the anisotropy of the surface free energy [18]. For a low-energy surface orientation, this corresponds to a reduction of Γ , and hence lower ϵ_c and easier roughening with increasing temperature. Above the faceting temperature the barrier E_s vanishes [18]. This is the case which has been treated previously [12]. Thus in high-temperature growth, surface roughness may occur even for modest misfit, while low temperature typically gives the maximum value of ϵ_c . To check this we examined films grown at 500°C instead of 560°C . At 30% Ge these films did not roughen, but relaxed by MFR, confirming that higher temperature facilitates roughening relative to other relaxation mechanisms. At 40% Ge, however, films roughened even at the lower

temperature.

Besides growing at low temperature or using surfactants, another powerful method of suppressing roughness is compositional grading. If one grows $\text{Si}_{1-x}\text{Ge}_x$ on Si, gradually increasing x from zero to the desired value, the film will begin to relax at a relatively low misfit. If the grading is sufficiently gradual, the continuous relaxation will prevent the strain from ever becoming large enough to initiate roughening [29]. We believe this is one reason for the reduced density of threading dislocations observed in graded layers.

In conclusion, we have presented compelling evidence that strain-induced surface "roughening" is the dominant mechanism for the introduction of dislocations in strained layers at high misfit, but this mechanism becomes kinetically unfavorable at low misfit. By enhancing or suppressing strain-induced surface roughening, using temperature, surfactants, or compositional grading, one can completely change both the surface morphology and the mode of relaxation.

This work was supported in part by ONR Contract No. N00014-92-00085.

-
- [1] J. H. van der Merwe, *J. Appl. Phys.* **34**, 117 (1963); **34**, 123 (1963).
- [2] J. W. Matthews and A. E. Blakeslee, *J. Cryst. Growth* **29**, 273 (1975); **32**, 265 (1976).
- [3] S. V. Kamat and J. P. Hirth, *J. Appl. Phys.* **67**, 6844 (1990).
- [4] E. A. Fitzgerald *et al.*, *J. Appl. Phys.* **65**, 2220 (1989).
- [5] P. M. J. Maree *et al.*, *J. Appl. Phys.* **62**, 4413 (1987).
- [6] D. J. Eaglesham *et al.*, *Philos. Mag.* **59**, 1059-1073 (1989).
- [7] D. D. Perovic and D. C. Houghton, in *Mechanisms of Heteroepitaxial Growth*, edited by M. F. Chisholm, B. J. Garrison, R. Hull, and L. J. Schowalter, MRS Symposia Proceedings No. 263 (Materials Research Society, Pittsburgh, 1992).
- [8] F. K. LeGoues, B. S. Meyerson, J. F. Morar, and P. D. Kirchner, *J. Appl. Phys.* **71**, 4230 (1992).
- [9] W. Hagen and W. Strunk, *Appl. Phys.* **17**, 85 (1978).
- [10] M. A. Capano, *Phys. Rev. B* **45**, 11 768 (1992).
- [11] W. H. Yang and D. J. Srolovitz, *Phys. Rev. Lett.* **71**, 1593 (1993).
- [12] D. Srolovitz, *Acta Metall.* **37**, 621 (1989); M. A. Grinfeld, *Sov. Phys. Dokl.* **31**, 831 (1986); R. J. Asaro and W. A. Tiller, *Metall. Trans.* **3**, 1789 (1972).
- [13] B. G. Orr, D. Kessler, and C. W. Snyder, *Europhys. Lett.* **19**, 33 (1992); C. W. Snyder, J. F. Mansfield, and B. G. Orr, *Phys. Rev. B* **46**, 9551 (1992).
- [14] B. J. Spencer, P. W. Voorhees, and S. H. Davis, *Phys. Rev. Lett.* **67**, 3696 (1991).
- [15] A. J. Pidduck, D. J. Robbins, A. G. Cullis, W. Y. Leong, and A. M. Pitt, *Thin Solid Films* **222**, 78 (1992).
- [16] David Vanderbilt and L. K. Wickham, in *Evolution of Thin-Film and Surface Microstructure*, edited by C. V. Thompson, J. Y. Tsao, and D. J. Srolovitz, MRS Symposia Proceedings No. 202 (Materials Research Society, Pittsburgh, 1991), p. 555.
- [17] D. E. Jesson, S. J. Pennycook, J.-M. Baribeau, and D. C. Houghton, *Phys. Rev. Lett.* **71**, 1744 (1993); see also, e.g., *Cavities and Cracks in Creep and Fatigue*, edited by J. Gittus (Applied Science, London, 1981).
- [18] As long as steps have a positive free energy of formation, the equilibrium crystal shape is faceted, and any small modulation of the surface has an energy cost which is linear in the modulation amplitude. This leads to a metastable strained layer, with an energy barrier to strain-induced morphological changes. In contrast, above the faceting temperature the step free energy vanishes [see M. Wortis, in *Chemistry and Physics of Solid Surfaces VII*, edited by R. Vanselow and R. F. Howe (Springer-Verlag, Berlin, 1988), p. 367]. Then the surface energy is quadratic in the modulation amplitude, given a barrierless instability as in the isotropic model of Ref. [12]. Strain modifies the energetics, possibly affecting the relative stability of different facets and so making the minimum-energy shape size dependent; but faceting is not eliminated in equilibrium except by high temperature.
- [19] P. Nozières and F. Gallet, *J. Phys. (Paris)* **48**, 353 (1987).
- [20] Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, *Phys. Rev. Lett.* **65**, 1020 (1990); D. J. Eaglesham and M. Cerullo, *Phys. Rev. Lett.* **64**, 1943 (1990); M. Horn-von Hoegen, B. H. Müller, A. Al-Falou, and M. Henzler, *Phys. Rev. Lett.* **71**, 3170 (1993); M. Horn-von Hoegen *et al.*, *Phys. Rev. B* **49**, 2637 (1994); A. Sakai and T. Tatsumi, *Phys. Rev. Lett.* **71**, 4007 (1993).
- [21] M. A. Lutz and R. M. Feenstra (unpublished).
- [22] J. Tersoff and R. M. Tromp, *Phys. Rev. Lett.* **70**, 2782 (1993).
- [23] The approximations underlying Eqs. (2) and (3) are discussed in Ref. [22]. In particular, we note that unless $s \gg h \cot \theta$, there are non-negligible errors associated with the treatment of the corners. For example, while the volume is formally treated as being $V = sth$, when $s = h \cot \theta$ the actual volume is 4/3 of this. Nevertheless, the scaling with size, misfit, etc., are given correctly, so our conclusions (which are qualitative rather than quantitative in nature) are unaffected by the approximation.
- [24] F. K. LeGoues, P. M. Mooney, and J. Tersoff, *Phys. Rev. Lett.* **71**, 396 (1993); P. M. Mooney, F. K. LeGoues, J. Tersoff, and J. O. Chu, *J. Appl. Phys.* (to be published).
- [25] F. K. LeGoues, J. Tersoff, and R. M. Tromp, *Phys. Rev. Lett.* **71**, 3736 (1993).
- [26] J. C. P. Chang, B. K. Kad, S. R. Nutt, and K. L. Kavanagh, *Mater. Res. Soc. Symp. Proc.* **312**, 107 (1993); L. J. Schowlater *et al.*, *Mater. Res. Soc. Symp. Proc.* **263**, 485 (1992).
- [27] In general, a lower surface energy would appear to favor roughening, see C. W. Snyder and B. G. Orr, *Phys. Rev. Lett.* **70**, 1030 (1993). However, for the faceted case with small facet angle θ , the difference $\gamma_e - \gamma_s$ between the surface energies of the different orientations is much more important than the absolute magnitude of the surface energy.
- [28] F. K. LeGoues, M. Copel, and R. M. Tromp, *Phys. Rev. Lett.* **63**, 1826 (1989); *Phys. Rev. B* **42**, 11 690 (1990).
- [29] J. Tersoff, *Appl. Phys. Lett.* **62**, 693 (1993).

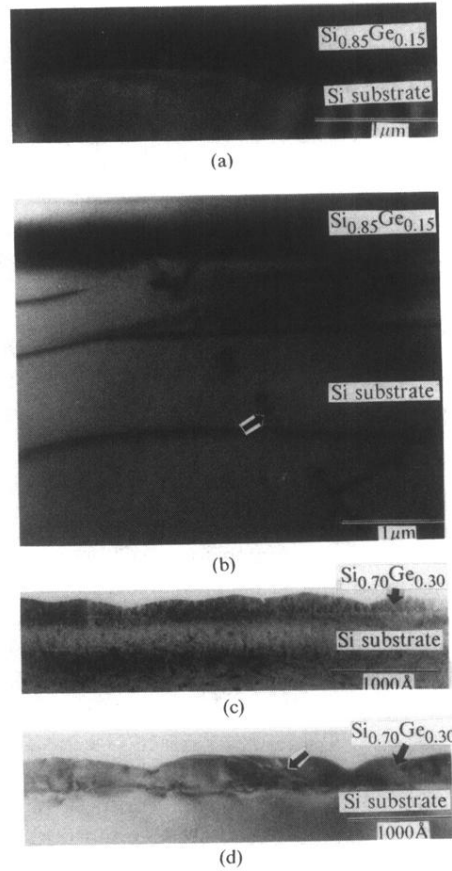


FIG. 4. Cross-sectional TEM images of $\text{Si}_{1-x}\text{Ge}_x$ films grown at 560°C on $\text{Si}(100)$, as described in text. Note different scales. (a) 5000 \AA layer at 15% Ge. The surface is flat, and no dislocations have formed. (b) 6500 \AA layer at 15% Ge. The surface is flat, and dislocations have been introduced by the MFR mechanism, as evidenced by the pileup of dislocations deep in the Si substrate. Arrow indicates one dislocation in the pileup. (c) 200 \AA layer at 30% Ge. The surface is rough, and no dislocations have formed. (d) 500 \AA layer at 30% Ge. The surface is rough, and the sample has relaxed. Arrow indicates one of the threading dislocations visible in the film.