Step-flow growth on strained surfaces

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A theoretical study is presented of the effect of misfit strain on the transition from step flow to island nucleation dominated epitaxial layer growth on a vicinal surface. The analysis generalizes a set of reaction-diffusion equations used for homoepitaxy to include the fact that heteroepitaxial strain changes the Arrhenius barrier for diffusion and promotes the detachment of atoms from the edge of strained terraces and islands. The first effect is equivalent to changing the deposition flux; the latter can drive the system into a new layer growth mode characterized by moving steps that engulf very many very small islands. Experiments to test these predictions are suggested.

In situ diffraction studies of homoepitaxial growth of GaAs(100) onto vicinal surfaces by molecular beam epitaxy,[1] metalorganic molecular beam epitaxy,[2] and metalorganic vapor phase epitaxy[3] all demonstrate the existence of a transition as a function of temperature and/or deposition flux from so-called *step-flow* layer growth to a layer growth mechanism dominated by the nucleation of two-dimensional (2D) islands. Theoretical analysis of this phenomenon has provided insight into the kinetics of epitaxial growth[4,5] and guidance to more practical growth studies that make use of step flow to fashion quantum wire epitaxial architectures.[6,7] Accordingly, we are motivated by the recent demonstration that step flow can be achieved even in the case of heteroepitaxy (AlSb/GaSb)[8] to present here a simple theoretical study of the effect of epitaxial strain on this transition. As will become apparent, our emphasis and methodology differ substantially from existing Monte Carlo computer simulation studies of the effect strain on epitaxial growth onto *singular* surfaces.[9]

The original analysis of step flow by Burton, Cabrera, and Frank (BCF)[10] focused on the steady-state distribution of adatoms that reflects the balance between deposition onto the terraces and adatom diffusion and incorporation at the vicinal terrace edges. To study the growth mode transition described above, Myers-Beaghton and Vvedensky[11,12] and Fuenzalida[13] supplemented the BCF driven diffusion equation for monomers with additional terms familiar from rate-equation theory[14] to describe the nucleation, growth, and dissolution of 2D islands (dimers, trimers, etc). Neglecting numerically insignificant terms, these authors show that the steady-state areal concentration of mobile adatoms, $n(x)$ and of immobile 2D islands composed of i atoms, $n_i(x)$, across a terrace of width l are determined by the following set of coupled nonlinear differential equations:

$$D\frac{d^2n}{dx^2} = -J - v\frac{dn}{dx} + 2Dn^2 + Dn\sum_{i=2}^{\infty}n_i - 2k_2n_2$$
$$- \sum_{i=3}^{\infty}k_in_i, \tag{1}$$

$$v\frac{dn_i}{dx} = -Dnn_{i-1} + Dnn_i - k_{i+1}n_{i+1} + k_in_i \quad (i>2). \tag{2}$$

In writing these equations (and in what follows), we set the lattice constant equal to one and assume that the density of kinks at each terrace edge is large enough so that the diffusion problem may be regarded as one dimensional.[10] Otherwise, J is the deposition flux, $v=Jl$ is the velocity of the advancing step edge, the surface diffusion constant $D=v\exp(-E_D/k_BT)$ fixes the rate at which diffusing adatoms *attach* to islands of any size,[14] and k_i denotes the rate at which individual adatoms *detach* from the edge of islands of size i. The boundary conditions that complete the specification of the problem are[12]

$$D\frac{dn}{dx}\bigg|_{x=0} = k_+n(0) - k_-n_s, \tag{3}$$

$$D\frac{dn}{dx}\bigg|_{x=l} = -k_+n(l) + k_-n_s, \tag{4}$$

$$n_i(l) = 0 \quad (i>2), \tag{5}$$

where n_s is the density of atoms singly bonded to a terrace edge, $k_+ = \frac{1}{4}D$ is the rate of adatom attachment to a step edge, and k_- is the rate for adatom detachment from a step edge.

To date, this formalism has been used to study the growth mode transition during homoepitaxy with the choices $k_i = \frac{1}{4}D\exp(-E_N/kT)$ and $K_-n_s = K_i\exp(-E_N/kT)$, where E_N is a parameter that characterizes a lateral pair bond energy.[12] As a check, we reproduce first the results of Ref. 12 by solving Eq. (1)–(5) assuming $E_N/E_D = 0.3$, $l = 20$, and a maximum island size of 10. For the indicated flux values, Fig. 1 illustrates the steady-state total number of atoms present in islands of various sizes on the terrace. Monomers dominate at the lowest flux and one is in conventional step flow. For the highest flux, one is in the nucleation region where large islands dominate. Since the steady-state model we use breaks down in this region[15] we focus below on the effect of heteroepitaxial lattice misfit on the transition region (white bars).

We generalize the foregoing to include the effect of misfit strain by supposing that the diffusion constant D as well as the detachment rate coefficients k_- and k_i depend explicitly on strain. The two effects will be discussed separately and then in concert. Regarding the former, we are aware of two molecular dynamics simulations addressed to quantifying the effect of strain on pure surface diffusion.[16]
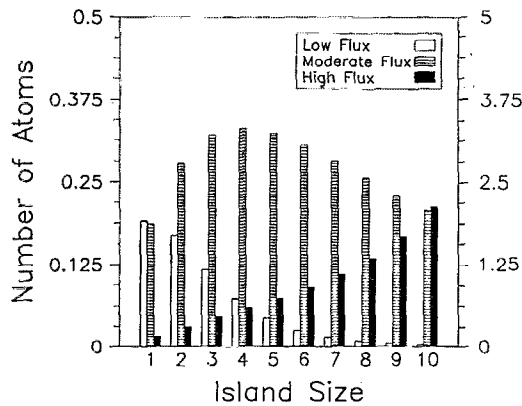
FIG. 1. The total number of atoms in each 2D island species on the terrace for $E_D/kT = 18.4$, no misfit and a flux of 1 ML/s (white bars), 0.57 ML/s (striped bars), and 1.73 ML/s (black bars). The scale on the left (right) corresponds to moderate and low (high) flux. The same result was obtained for $E_D/kT = 18.4$, a flux of 1 ML/s and a decrease (striped bars) and increase (black bars) of E_D by $\sim$3.3% for 4% misfit.

Unfortunately, these studies do not reveal any simple physical argument that predicts even the *sign* of changes to the Arrhenius barrier E_D for semiconductors. We therefore discuss both possibilities. This is quite simple because an examination of the defining equations of motion above reveals that every term depends linearly on either D or the deposition flux J. Hence, an increase (decrease) of E_D due to misfit strain corresponds *exactly* to an appropriate increase (decrease) in flux. The bar graphs in Fig. 1 are reinterpreted similarly. When strain increases (decreases) the rate of surface diffusion, more (fewer) atoms reach the terrace edge and the system is driven away from the transition region and toward the step-flow (nucleation) region.

Consider next the isolated effect of strain on the detachment rate coefficients. The basic idea here is that the effective binding energy for *every* atom in a strained island or terrace is reduced with a concomitant reduction in the Arrhenius energy barrier for detachment of atoms. We choose

$$k_i = \frac{1}{4} D \exp\left(-\frac{E_N - E_{\text{strain}}(i)}{kT} \right) \qquad (6)$$

and $k_- = k_{i \to \infty}$ where $E_{\text{strain}}(i)$ is the strain energy/atom of a 2D epitaxial island composed of i atoms.[17] We approximate the barrier reduction due to strain as $E_{\text{strain}}(i) = 2\bar{E}_{\text{strain}}(\sqrt{i})$, where $\bar{E}_{\text{strain}}(i)$ is the strain energy/atom of a *one-dimensional* chain of i harmonically coupled atoms in contact with a rigid sinusoidal potential. This model possesses two great virtues for our purposes: the quantity $\bar{E}_{\text{strain}}$ is known analytically[18] and it captures correctly the important phenomenon of lateral strain relaxation near the edges of epitaxial islands. In particular, very small islands are essentially unstrained. The model parameters are chosen to reproduce the elastic and cohesive properties of typical semiconductor materials.[19]

Figure 2 illustrates the steady-state total number of adatoms and atoms condensed into islands of various sizes under various conditions. At zero strain (white bars), we
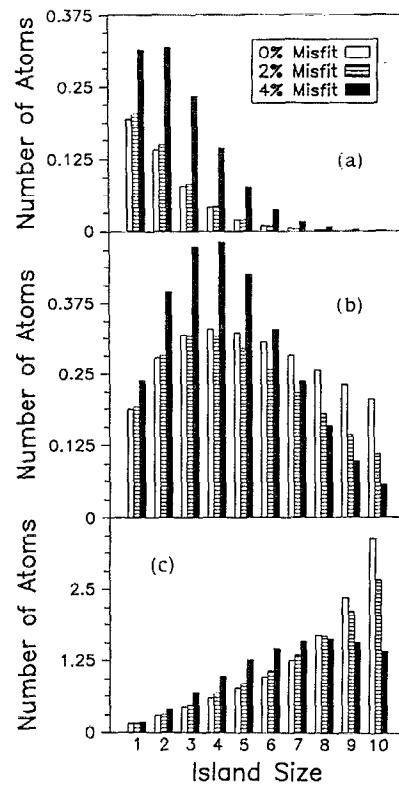

FIG. 2. The total number of atoms in each 2D island species on the terrace as a function of temperature for three different values of epitaxial misfit strain. (a) Step flow: $E_D/kT = 17.8$; (b) transition region: $E_D/kT = 18.4$; (c) nucleation region: $E_D/kT = 19.0$. Note the different vertical scales.

very nearly[20] reproduce the results shown in Fig. 1. Consider the transition region [Fig. 2(b)]. When strain first is introduced, the Arrhenius barrier to adatom detachment is reduced more for large islands than for small islands with a concomitant decrease in number densities of the former. Of course this barrier is most reduced at the step edge,[21] but for small strains, adatom detachment there cannot overcome the energy gain of incorporation into the bulk of the solid that is implied by the steady-state advance of the step. This is not so for the islands, some of which grow and some of which shrink in order to maintain the steady state. As the strain increases, the concentration of small (essentially unstrained) islands increases rapidly as detachment from the vicinal step edges ensues. One thus observes a strain-dependent critical island size i^*: when $i < i^*$ ($i > i^*$), n_i increases (decreases) compared to the zero-strain case. It is clear from Fig. 2(b) that more nearly step-flow conditions obtain in the transition region for a moderately strained system than for an unstrained system. Larger strain apparently drives the system away from conventional step flow and into a new mode of growth characterized by a step advancing almost exclusively by the incorporation of very many very small islands.

The two strain effects discussed above can be superimposed if we neglect the difference between changing flux and temperature. Figure 2 then can be reinterpreted as follows. Begin in the transition region without strain [Fig.

2(b), white bars]. If misfit strain *decreases* the Arrhenius barrier E_D, the system is driven toward island populations similar to those illustrated by the white bars in Fig. 2(a). The additional effect of strain on the detachment coefficients then drives the populations toward those indicated by the black bars in Fig. 2(a). The net result is a transition toward step flow with the additional feature that the vicinal step edges advance more by engulfing dimers and small islands than is the case for step flow in an unstrained system. Conversely, if strain *increases* the barrier to surface diffusion the two effects we have discussed tend to offset one another and the system may remain in the transition region. Nonetheless, we expect more small relaxed islands than in the homoepitaxy case.

All of the predictions of this study are amenable to experimental test. The disappearance of reflection high-energy electron diffraction (RHEED) oscillations as a function of temperature and/or deposition rate probably is the most straightforward monitor of the transition from island nucleation to step flow.[1,2] But this averaging technique does not clearly distinguish whether the transition is driven primarily by the influence of strain on D or on the adatom detachment coefficients. Scanning tunneling microscopy (STM) seems best suited for this purpose because the two effects affect the distribution of island sizes in different ways. The former ought to yield a distribution identical to the case of homoepitaxy[22] but shifted in deposition flux. The latter alters the distribution from the zero strain case. Direct correlation of such STM studies with RHEED[23] would be particularly valuable.

Several cautions must be noted for these purposes. First, growth must be confined to the first few monolayers of growth because, as is well known,[24,25] strain relief ultimately occurs by the destabilization of layer growth in favor of three-dimensional island formation. Second, one must be certain to isolate the effects of strain. Thus, a study of the step-flow to nucleation-dominated layer growth transition for GaAs growth onto various $In_xGa_{1-x}As$ substrates is to be preferred to a study of $In_xGa_{1-x}As$ growth onto GaAs substrates so that the fact that In atoms and Ga atoms have very different surface diffusion rates does not confuse the issue.[26]

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[21] This is so because we interpret the terraces as very large islands. There is no contradiction with the fact that elastic relaxation occurs at the step edges because the global driving force for strain-induced island dissolution can only manifest itself at step edges for small to moderate values of misfit.

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