Suppression of Intermixing in Strain-Relaxed Epitaxial Layers

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Misfit strain plays a crucial role in semiconductor heteroepitaxy, driving alloy intermixing or the introduction of dislocations. Here we predict a strong coupling between these two modes of strain relaxation, with unexpected consequences. Specifically, strain relaxation by dislocations can suppress intermixing between the heterolayer and the substrate. Monte Carlo simulations and continuum modeling show that the suppression, though not absolute, can be surprisingly large, even at high temperatures. The effect is strongest for a large misfit (e.g., InAs on GaAs) or for thin substrates (e.g., Ge on silicon on insulator).

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Since the early days of semiconductor heteroepitaxy, the role of misfit strain has been a constant theme. Initially the focus was on avoiding the relaxation of misfit strain by dislocations. More recently, strain-relaxed layers have shown great promise as templates with variable lattice spacing, enabling structures with dramatically strain-enhanced electron mobilities for high-performance transistors [1].

Strain can also be relaxed by intermixing of the two different-sized components, a process which blurs the heterointerface and so is highly detrimental for heterostructures. Intriguingly, these two modes of strain relaxation may couple [2]. This has been widely discussed in the context of ''strain-enhanced diffusion'' [3].

Here we show that these two modes of strain relaxation can couple in an entirely different way, with important implications for the thermal stability of strain-relaxed template layers. Specifically, strain relaxation by dislocations can suppress intermixing between the heterolayer and the substrate. Intermixing is suppressed because, once the strain is fully relaxed by dislocations, intermixing would actually increase the strain.

This assumes that any dislocations are immobile; and indeed, heterolayers that are almost fully relaxed by sessile dislocations have been reported for Ge on Si (001) [4] and InAs on GaAs (001) [5]. Thus systems already exist that would be sufficient for a proof of principle. (In these systems the relaxation was unintentional, and doubtless left high densities of threading dislocations, so further optimization would be needed to approach device-quality material.)

In order to demonstrate this effect and study it, we carry out Monte Carlo (MC) atomistic simulations. We also develop a continuum model based on classic principles [2], and we verify that it reproduces the MC results. In this way we can predict the extent and rate of intermixing in thin heterolayer films as a function of temperature, degree of relaxation, and other parameters. Our MC equilibrium results for Ge on effectively thin substrates like silicon on insulator (SOI) [6] show a significant suppression of alloying in the film. The effect is even stronger for InAs on GaAs, due to the larger misfit. Continuum modeling allows us to extend these results to very thick (effectively semi-infinite) substrates, where we find a dramatic slowing-down of intermixing over long times.

We consider first the equilibrium of an epitaxial layer on a substrate where intermixing is limited to a thin region, as for SOI substrates. We treat Ge on Si (001) and InAs on GaAs (001), in each case either coherent or relaxed by dislocations. The epilayers contain 60 Ge or InAs monolayers and are terminated by reconstructed (dimerized) surfaces. We allow equilibration within these 60 layers plus the first 238 layers of substrate, with deeper layers ''frozen'' to represent, e.g., the oxide in an SOI substrate. This corresponds to a substrate thickness of $\sim$32 nm, readily achievable with SOI. The lattice constants parallel to the layer are fixed by the epitaxial constrain of zero strain deep in the substrate, leaving the film under biaxial stress. The computational cells are periodically repeated in two dimensions.

For the relaxed case, we include one dislocation per cell in each direction, with sessile 90° (Lomer type) dislocations. The dislocation spacing is set by the cell size ($L \times L$), which is chosen here to correspond to nearly complete relaxation of misfit strain. The core structure is shown in Fig. 1, and it conforms with experimental observations [7]. We note that details of core structure and surface reconstruction do not affect the results presented here.

The system is allowed to equilibrate, both geometrically and compositionally, using a continuous-space MC method that has been extensively tested in similar environments [8–10]. Three types of random moves are involved in the MC algorithm: atomic displacements and volume changes, which lead to geometrical relaxation, and mutual identity

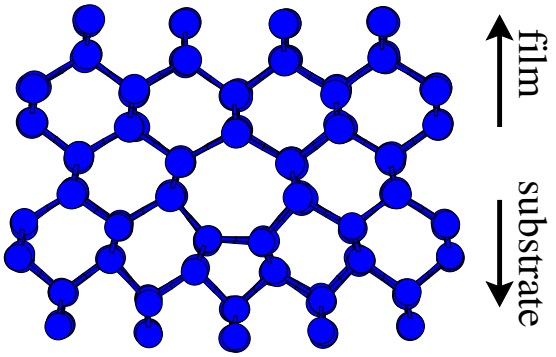

FIG. 1 (color online). Ball and stick model of a typical Ge/Si(001) structure with a Lomer dislocation (shuffle type) at the interface. The Burgers vector $\vec{b}$ lies in the (001) plane.

exchanges (Ising-type flips) between nearest-neighbor atoms of different kinds, which mimic atomic diffusion and lead to compositional equilibration throughout the system. The number of atoms of each species is kept constant. One starts with the initial configuration, a thin unalloyed layer on a thicker substrate, and the system is allowed to evolve to its equilibrium composition state by the identity exchange mechanism. The enthalpy is calculated using well-established interatomic potentials for Si/Ge [11] and InAs/GaAs [12].

We first present MC results for equilibrium at 300 K. This is somewhat artificial, since there is experimentally not enough bulk diffusion to equilibrate at this temperature, but it provides a useful reference case before addressing the dependence on temperature up to high temperatures.

Figure 2 summarizes the equilibrium properties of our Si/Ge and InAs/GaAs systems, showing the effect of dislocations in suppressing intermixing. Figure 2(a) shows local composition (Ge or In site occupancies) averaged over time and over thicknesses 0.63 nm and 1.03 nm, respectively. Without dislocations, the intermixing would be complete, corresponding to the black dashed line in Fig. 2(a). With dislocations, the suppression of intermixing between film and substrate is striking. We also note the spatial abruptness of the transition, occurring over just a few nanometers. This width reflects more complex segregation around the dislocation core [10], as well as the finite spacing between dislocations.

The effect can be understood by noting that, in a coherent system, intermixing not only increases the entropy, it also simultaneously reduces the strain energy. Thus the effect of strain is actually to increase the rate of intermixing. However, when the strain has been fully relaxed by sessile dislocations, any intermixing introduces strain into the relaxed system, raising the energy. This increase in energy opposes the increase in entropy, leading to a limited intermixing which minimizes the free energy between these competing effects.

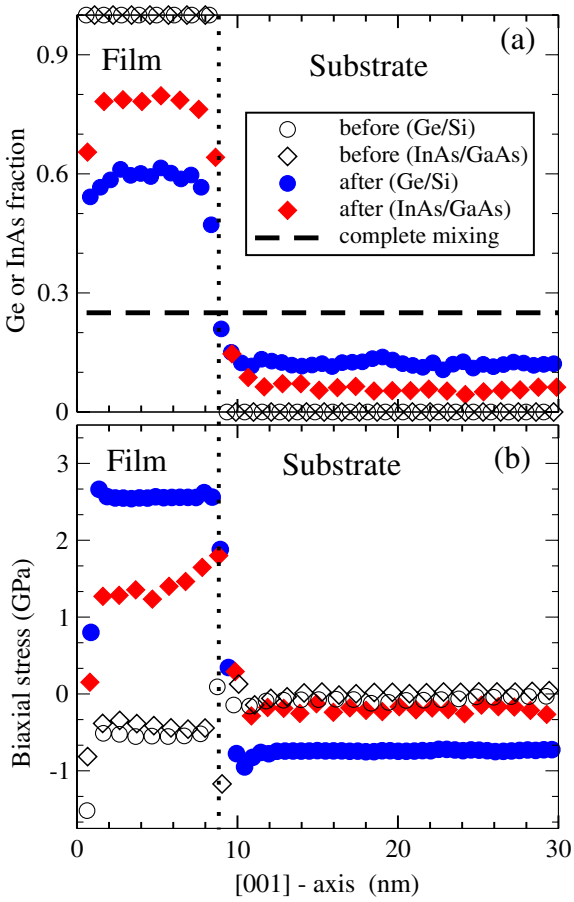

FIG. 2 (color online). Equilibrium composition and stress in our system at 300 K. (a) Composition variations along the [001] growth axis of Ge and InAs dislocation-relaxed films on thin Si and GaAs substrates, respectively, before and after intermixing, as indicated in the legend. Points denote local atomic compositions averaged over slices having thicknesses of ~0.63 nm (Ge/Si) and 1.03 nm (InAs/GaAs). Dashed horizontal line shows the limit of perfect mixing in the nondislocated case. Dotted vertical line denotes the interface position. (b) Biaxial stress at 300 K in the above structures, before and after intermixing. Points denote local atomic stresses averaged as in (a).

Suppression of intermixing is especially pronounced in the case of InAs/GaAs in Fig. 2, due to two factors: the larger size mismatch compared to the Ge/Si case; and the fact that only half the atoms (the group III cations) contribute to the entropy via intermixing.

Figure 2(b) shows atom-projected local stress [8], averaged as above, in the film and the substrate. Initially, before interdiffusion, the average atomic stress approaches zero, confirming that the misfit dislocations largely relieve the heteroepitaxial strain. (The stress is not exactly zero here, there is a small residual stress in the film because the misfit cannot be made exactly equal to the fractional lattice mismatch using one dislocation per cell.) However, significant stress develops during alloying due to the size mismatch between the mixing species. This depends on

the degree of intermixing and explains the larger stress in alloyed Ge/Si compared to InAs/GaAs.

Having demonstrated the effect at a low temperature, we now turn to higher temperatures that are relevant to experimental growth conditions. For this, we carried out a series of MC simulations at increasing temperatures, extracting each time the equilibrium composition in the heterolayer. The results are shown in Fig. 3. Significant suppression of alloying persists even up to quite high temperatures, e.g., ~50% InAs in the film at 900 K, and ~40% at 1500 K (not shown), where bulk diffusion is rapid.

In order to gain more insight into the interplay between dislocation and intermixing effects, we develop an analytic model for the thermodynamics and kinetics of these systems. The free energy density for composition c can be written as

$$F(c) = c(1-c)\Omega + TS + E_{\mathrm{el}}, \tag{1}$$

where Ω is the interaction parameter in regular-solution theory, E_{el} is the elastic energy density, and S is the entropy, approximated as for an ideal random solution, $S = k_B(c\ln(c) + (1-c)\ln(1-c))$. Then the average free energy density of the total system is

$$\langle F\rangle = \alpha F_f(c_f) + (1-\alpha)F_s(c_s), \tag{2}$$

where α is the number of atomic layers in the film, as a fraction of the total number of interdiffusing layers. Also c_f and c_s are the Ge (or In) composition in the two regions. These are obtained by free energy minimization, subject to the constraint of material conservation.

The elastic energy is $E_{\mathrm{el}} = \frac{1}{2}C_{ij}S_iS_j$ using the standard cubic convention $i = 1,\ldots,6$. We linearly interpolate alloy elastic constants between the elemental values. For our biaxially symmetric geometry, and zero stress normal to a free surface, the elastic energy becomes

$$E_{\mathrm{el}} = \frac{1}{2}[C_{11}(2S_1^2 + S_3^2) + 2C_{12}(S_1^2 + 2S_1S_3)]. \tag{3}$$

We use Vegard's law (linear interpolation) for alloy lattice constant. The substrate lattice spacing is a_s, while in the fully relaxed film it is $a_s(1+f)$, where f is the fractional misfit. Full relaxation implies dislocation spacing $L = b/f$, where b is the misfit component of the Burgers vector. Then the elastic energy densities for Eqs. (1) and (2) are

$$E_{\mathrm{el}}^{(f)} = \frac{(C_{11}-C_{12})(C_{11}+2C_{12})}{C_{11}}[(1-c_f)f]^2 \tag{4}$$

$$E_{\mathrm{el}}^{(s)} = \frac{(C_{11}-C_{12})(C_{11}+2C_{12})}{C_{11}}(c_sf)^2 \tag{5}$$

for the relaxed film and the substrate, respectively.

For the interaction parameter Ω in the chemical energy term, we use, for Ge/Si, the value 9 meV, obtained from first-principles calculations [13], while for InAs/GaAs we calculate it to be 11 meV, in agreement with previous work [12].

We use this model to calculate the temperature dependence of the equilibrium composition. The results are shown in Fig. 3. The model agrees well with the MC simulations, confirming our understanding of the mechanism for suppression of intermixing.

In device processing, the system is typically at high temperature for only a short time, so the degree of intermixing is limited even for a semi-infinite substrate. Then the issue is not equilibrium, but rather the rate of intermixing. To address this, we develop a simple one-dimensional kinetic model for interdiffusion. Assuming that no voids form, we have equal and opposite diffusion currents for the two species, obeying

$$j = -M(\nabla\mu_a - \nabla\mu_b) \tag{6}$$

$$M = \frac{m_bc_bm_ac_a}{m_ac_a + m_bc_b}. \tag{7}$$

Here m_a and m_b are the elemental mobilities, c_a and c_b are the respective concentrations, and μ_a and μ_b are the chemical potentials for each element, calculated numerically from Eq. (1). The mobility Eq. (7) is derived using the "network constraint" approach [14]. Here for simplicity we assume $m_a = m_b$, so $M = mc(1-c)$. In general, m may itself depend on composition and on stress. However, these dependences are not well understood, and they are expected to be small corrections to the effects discussed here, so we omit any such dependence. (We also neglect such effects in the MC model.)

We obtain the spatial and time evolution of the composition by solving, through discretization, the continuity

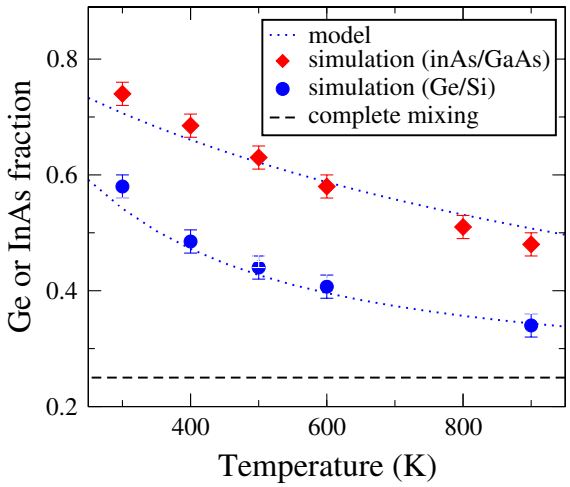

FIG. 3 (color online). Dependence of Ge and InAs fraction in heterolayer on temperature. Filled symbols and dotted lines denote MC simulation and model results, respectively. Horizontal dashed line shows expected composition in coherent films.

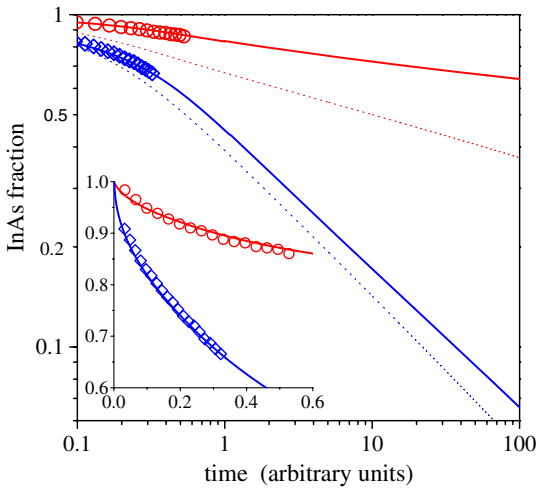

FIG. 4 (color online). Evolution of composition in InAs film on GaAs. Diamonds and circles are MC results for coherent and dislocation-relaxed layers, respectively. Solid curves are model results for the semi-infinite substrate. Inset emphasizes early-time behavior for comparing the model and MC results. Time units are arbitrary, with the mobility m scaled to best match the MC results. Temperature is 300 K. Model results for 900 K are shown as dotted lines for comparison (horizontal alignment is arbitrary due to different time units at different T).

equation $\partial c(z,t)/\partial t = -\nabla j$, with the flux given by Eq. (6). We explicitly allow for a discontinuity in the plane of the dislocations. The rate of intermixing is monitored through the evolution in time of the film composition (Ge or InAs fraction). We confirm that the solution of the equation at the long-time limit yields a composition in excellent agreement with the thermodynamic model.

For an InAs thin film on an effectively infinite GaAs substrate, the composition evolution over time is shown in Fig. 4. At long times, the composition of a coherent film decays approximately as $t^{-1/2}$, consistent with simple diffusion. This is reasonable, because at increasing dilution, strain becomes unimportant as a driving force. In contrast, the rate of mixing is greatly retarded in the strain-relaxed film. For example, at $t = 37$ the composition in the film has decayed to 10% In in the coherent case. But with relaxation of the strain by dislocations, the composition is still 68% In after the same time, and is decaying an order of magnitude more slowly.

Figure 4 also shows results of the MC simulation. These are limited to shorter times, where no appreciable diffusion has reached the cell boundary. Thus the results may be directly compared with a semi-infinite substrate. Choosing m to match the overall time scale, we find excellent agreement between the continuum model and MC simulations for both strained and relaxed layers.

Finally, we emphasize that the thermodynamic and kinetic models can be readily applied for the optimization of devices. One can predict the dislocation and thin film parameters (density, type, thickness) necessary to achieve the desired alloying and stress field, for different types of lattice-mismatched heterostructure, such as SOI structures with finite substrate thickness, and also predict the rate of alloying at various temperatures. Given the large number of parameters available, this optimization would not be feasible by direct simulation.

In conclusion, Monte Carlo simulations and continuum modeling have been used to study the coupling between intermixing and dislocation fields in heterolayer systems. It is shown that intermixing is greatly retarded for systems relaxed by misfit dislocations. The effect, which is of interest not only for planar layers, but also for any structure relaxed by dislocations, including islands and other nanostructures, opens new possibilities for the control of stress and property optimization in semiconductor devices.

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