A mechanism for liquid-phase epitaxial growth of nonequilibrium compositions producing a coherent interface

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A model is presented for growth by so-called composition pulling, wherein an epitaxial deposit grows coherently but with a composition different from that which would be in bulk equilibrium with the liquid phase from which growth occurs. The breakdown of coherent growth occurs when a dislocation nucleates at a ledge at the growing solid-liquid interface. An expression for the critical condition for breakdown is presented.

In a study of growth of $Ga_xIn_{1-x}P$ by LPE on a GaAs substrate, Stringfellow[1] observed that growth from liquids with a range of compositions produced the same solid composition. Liquids within about $\pm 10\%$ of the zero-lattice-parameter composition yielded solid with $x = 0.51$, the zero-lattice-parameter mismatch composition. Other reports have confirmed this effect in the Ga-In-P system[2,3] and in the Ga-As-Sb and In-As-Sb systems,[4] as well as in such dissimilar systems as magnetic garnet materials grown from a flux.[5] However, in the quaternary system Ga-In-As-P, the effect is not observed.[6,7]

Stringfellow[1] attempted to calculate the magnitude of the effect by computing the free energy of the nearly lattice-matched overgrowth, determining the minimum free-energy composition including strain-energy terms and chemical terms. Reduction in the strain-energy contribution was found to offset the increase in the chemical contribution in this model. The observed variation of nearly lattice-matching composition with liquid composition was found to agree very well with the model.

The ultimate breakdown to a dislocation interface was also rationalized by a free-energy argument. For large enough mismatch, the free energy of a dislocated overgrowth of equilibrium composition was computed to be less than the lattice-matching overgrowth. Again, the computed transition composition agreed well with the computations. However, the dislocation energy was probably overestimated because of neglect of image stresses, so the latter part of the correlation is in question.

Here, we suggest a kinetic model for the ultimate breakdown, which nevertheless retains the thermodynamic portion of the correlation when lattice matching occurs.

In the deposition of a one-component epitaxial overgrowth on a substrate with near lattice matching, the initial nuclei are coherent because the attendant reduction in surface energy offsets the strain energy in the nucleus.[8-10] As the nuclei grow they can become semi-coherent in several ways. For lateral growth, nucleation of an interface dislocation at the periphery of the nucleus becomes favorable for large particles, and dislocations are injected, reducing the strain energy and creating lattice mismatch.[8,9] For thick overgrowth, dislocations can also be injected from the free surface.[11] However, image forces prevent this injection below a critical thickness of the order of $1-2$ nm.[12]

For growth from a multicomponent system, such as Ga-In-P, an alternative model is possible. Again the nucleus should be coherent. Now as growth occurs, however, rather than accumulating elastic strain energy, the particle can initially grow with nearly lattice-matching composition as suggested by Stringfellow.[1] This form of growth greatly suppresses the probability of dislocation nucleation and permits growth of macroscopic coherent lattice-matching overgrowths.

The ultimate breakdown in such coherent overgrowth is then supposed to be dislocation nucleation controlled in a ledge-type growth model.[13] The observations reported by Strauss[7] for growth of Ga-In-As-P, indicating more rapid growth of (100) surfaces than for (111) surfaces having the same temperature dependence of growth, strongly suggest such a ledge-type model. As atoms attach at kink sites on ledges, the strain-chemical free-energy model applies locally and atoms are selected to reduce local strain buildup of the type shown in Fig. 1. With sufficient chemical driving force, the nucleation of a dislocation loop, as shown in Fig. 2, will eventually lead to breakdown of the coherent interface.

Conventional nucleation theory[10] indicates that the free energy of such a configuration is

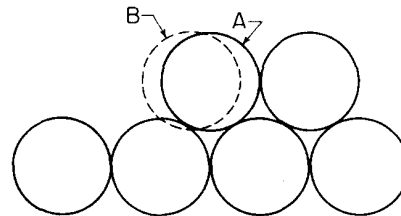$$\Delta G = (l/b)\Delta G + \tfrac{1}{10}\mu b^2 l + \mu b^4/l, \tag{1}$$

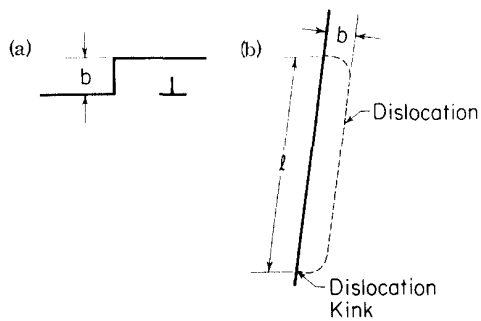FIG. 1. Atom being added at a ledge. A: unstrained configuration; B: locally strained configuration.

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FIG. 2. Dislocation being created at a ledge: (a) cross-sectional view, (b) view normal to solid-liquid interface.

where ΔG is the negative chemical free-energy difference per atom between solid of equilibrium bulk composition and solid of lattice-matching composition, l is defined in Fig. 2, b is the lattice spacing, $\frac{1}{10}\mu b^2$ is the roughly core-type energy per unit length of such a dislocation, and $\mu b^4/l$ is the interaction energy between the dislocation kinks at the ends of the length l. Minimization of the free energy with respect to l gives a critical length

$$l^* = \left(\frac{\mu b^5}{\frac{1}{10}\mu b^3 + \Delta G}\right)^{1/2} \qquad (2)$$

and a critical free energy

$$\Delta G^* = 2(\mu b^3)^{1/2}(\tfrac{1}{10}\mu b^3 + \Delta G)^{1/2}. \qquad (3)$$

Theory predicts nucleation when

$$\Delta G^* = kT \ln(n\nu/J), \qquad (4)$$

where $n = 2.5\times 10^9$ m^{-1} is the number of sites per meter of ledge, $\nu = 10^{13}$ s^{-1} is the atomic vibration frequency (the attempt frequency for nucleation of a loop), and $J \sim 10^2$ m^{-1} s^{-1} is the critical observable nucleation rate required for nucleation. Substituting Eq. (4) into Eq. (3) gives a prediction of ΔG required for nucleation as a function of known parameters. For Ga-As-P grown on Ga-As, with the use of the value $\mu = 3.39\times 10^{10}$ Pa from the work of Hakki *et al.*,[14] $b = 0.4$ nm, and $T = 1060$ K, this procedure yields a value of ΔG of -97.9 kJ/mole. In terms of the computations of Stringfellow[1] for this system, this corresponds to the free-energy difference between solids with $x = 0.31$ or 0.71 and the

lattice-matching solid with $x = 0.51$. These predicted values of $\Delta x = 0.20$ at which the epitaxial layer growing on a Ga-As substrate should become noncoherent compare with an experimentally observed value of $\Delta x = 0.11$.

Thus, there is only fair agreement between expectation and experience, but it is reasonable in view of the approximations in the above estimates. The dominant factor in the predicted values is the core energy: a value of $\frac{1}{27}\mu b^3$ (much smaller because of the nonlinear relation between ΔG and Δx) would be required for this parameter to give perfect agreement. Core energies this small are possible, but to resolve the parameter more accurately than above, atomic calculations, including surface-image effects, would be rquired for the nonlinear elastic core-type configuration shown in Fig. 2.

ACKNOWLEDGMENT

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