Asymmetric Tilt Boundaries and Generalized Heteroepitaxy

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In conventional heteroepitaxy, lattice mismatch is accommodated through biaxial strain and interfacial misfit dislocations. In studies of the heterophase boundaries appearing in semicoherent α-Si_3N_4 precipitates grown *in situ* in a silicon matrix, we have found that part of the lattice mismatch can be accommodated by formation of low-energy asymmetric tilt boundaries, which accommodate the lattice mismatch without producing a long-range stress field. This result suggests that growth of misfit-dislocation-free lattice-mismatched tilted structures should be possible.

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Epitaxy describes a condition in which adjoining crystals have a definite relative orientation, with low-energy interfacial structures being favored.[1] Low-energy interfaces are often discussed in terms of simple geometric criteria based on structural coincidences between the adjoining crystal lattices. Consider a symmetric tilt boundary between two half spaces of the same crystal. If the tilt is zero, all of the interfacial sites are exactly coincident. In this case, any dislocations in the interface must have Burgers vectors characteristic of the crystal lattice. In the case of general symmetric tilts, however, there will be few or no coincident sites. The result is a high-energy interface containing a mix of intrinsic and extrinsic dislocations. (A "pure" interface having no long-range stress field will be composed of intrinsic dislocations. Any additional dislocations will produce long-range stresses, and are called extrinsic.) For certain special tilt angles, however, a significant fraction of the interfacial sites will be coincident. Near these orientations, an interfacial dislocation dissociates into intrinsic secondary grain boundary dislocations. These dislocations have Burgers vectors not corresponding to the crystal lattice, but rather to the displacement shift complete lattice, which for simple cubic crystals is the reciprocal lattice of the lattice defined by the coincident sites between the two tilted crystals. Because secondary grain boundary dislocations have smaller Burgers vectors (and hence much smaller core energies) than do the crystal lattice dislocations, and intrinsic dislocations do not produce a long-range stress field, these symmetric tilt boundaries with special orientations are often very low in strain energy.

As discussed by Sutton and Balluffi,[2] the low-energy geometric criterion with the broadest generality requires a large and spatially periodic density of coincident interfacial sites. When heterostructures are considered, however, it is rare to find orientations which yield a high density of exactly coincident sites. Despite this, in many cases a low-energy interface can still be formed.[3] First, a relative misorientation is found which produces an appropriate distribution of nearly coincident interfacial sites. The crystals are then subjected to body stresses which force coincidence of the interfacial sites. These body stresses must then be canceled by introduction of a network of interfacial (misfit) dislocations to remove long-range stress fields. Local atomic relaxation then yields the low-energy interphase boundary structure. Heterointerfaces constructed in this manner are often low in energy compared with a general high-angle grain boundary.

An interesting class of interphase boundaries are those formed during heteroepitaxial growth of lattice mismatched but structurally similar materials. There are two distinct cases of interest for microelectronic applications. For layers thinner than a critical thickness h_c, the lattice mismatch can be accommodated by forming coherent interfaces, producing strained-layer structures.[4] Formation of coherent interfaces between lattice-mismatched structures requires imposition of a biaxial strain in the interfacial plane, to which the biaxially constrained material reacts by straining (via the Poisson effect) in the perpendicular direction. (Although stability in the presence of body strains appears contrary to the prescription for near-coincidence structures, the finite thickness of the strained layer allows the strain energy of the coherent structure to be less than that required to introduce misfit dislocations at the interface.) In contrast, for layers thicker than h_c, the mismatch is accommodated by a combination of biaxial strain and an interfacial misfit-dislocation network in the fully relaxed structure. These considerations apply to multilayer structures as well as simple overlayers.[5]

An important application of relaxed heterostructures involves growth of III-V semiconductors (e.g., GaAs) on silicon substrates.[6] Such structures would combine the superb electronic properties of the III-V semiconductors with the ease of fabrication and high device density possible in silicon microelectronics. Unfortunately, fabrica-

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tion of high-quality III-V/Si structures is not currently practical. Interaction of misfit dislocations with interfacial defects produces a large density of threading dislocations in the GaAs layer.[7] Accordingly, if accommodation of lattice mismatch could be accomplished without introduction of misfit dislocations, it would not only offer new insights into the physics of interphase boundaries, but might also have significant practical applications.

A simple geometrical construction (Fig. 1) suggests that asymmetric tilt boundaries can benignly accommodate lattice mismatch. For simplicity, we consider mismatch along only one lattice direction. These ideas generalize readily to biaxial mismatch in general cubic lattices, as well as special combinations of tetragonal and/or orthorhombic crystals. For example, if an interface at a (100) cubic surface having biaxial mismatch is desired, the overlayer would simply be tilted about an [110] axis to accommodate the mismatch. There are, however, families of crystal structures (e.g., hexagonal) for which asymmetric tilt boundaries are not capable of accommodating general lattice mismatch.

At an asymmetric tilt boundary, the effective mismatch goes to zero at an accommodation angle θ_0 defined by $a_0\epsilon_0/a_1 = 1 - \cos\theta_0$, where $\epsilon_0 = (a_1 - a_0)/a_0$ is the lattice mismatch. In order to avoid long-range stress fields, however, the overlayer tilt must result from a rigid rotation, rather than reflecting a bulk shear strain. The resulting interface will generally present a periodic network of intrinsic interfacial dislocations with Burgers vectors perpendicular to the tilted interface [Fig. 1(b)]. This type of structure is the analog of the symmetric tilt boundary in homophase structures, and leads to effective cancellation of the long-range dislocation strain fields.[8] Asymmetric tilt boundaries thus present another possible low-energy route toward accommodation of lattice mismatch in heteroepitaxy.

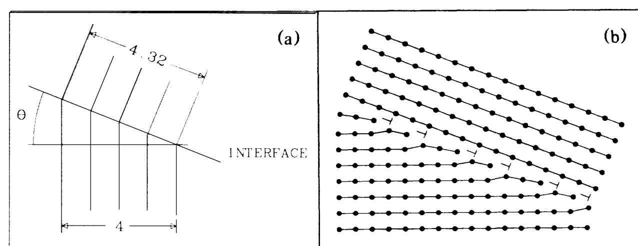

FIG. 1. Accommodation of lattice mismatch by formation of asymmetric tilt boundaries. (a) A schematic demonstrating that lattice tilt allows the interplanar spacings of two lattices having 8% mismatch to coincide at the tilted interface. (b) A schematic view of a similar interface between two mismatched cubic lattices, where the substrate surface is indicated by the stepped line. The atomic relaxation required to change untilted and strained overlayer growth on the substrate ledges to growth of a tilted, but unstrained, overlayer appears clearly.

Evidence that asymmetric tilt boundaries can play an important role in accommodation of lattice mismatch has arisen in our studies of the interphase boundaries which form when silicon nitride precipitates are grown *in situ* within a silicon matrix.[9] Samples are prepared by 150-keV N^+ implantation of a (110) silicon surface, followed by high-temperature annealing. The resulting α-Si_3N_4 precipitates take the form of semicoherent lenticular plates roughly 100 nm across and 50 nm thick, oriented so that the top and bottom surfaces of the plate are α-Si_3N_4(0001)/Si(111) interfaces. Despite a lattice mismatch of about 0.6%, this interface is coherent, in agreement with models for strained-layer epitaxy.[10]

Based on the model discussed earlier, interfacial tilt should reduce the strain energy of the Si_3N_4 precipitates. Further, when semicoherent precipitates are grown *in situ,* the symmetry constraints presented by the original matrix are partially disrupted during the growth process. As a result, the precipitate can rotate relative to the matrix, if this reduces the total energy of the system. In Fig. 2 a high-resolution transmission electron micrograph image of the coherent Si_3N_4(0001)/Si(111) interface appears which shows that the Si_3N_4(0001) planes are tilted by 5–10 mrad relative to the (111) planes of the Si matrix, in agreement with Moire fringes on the precipitate sides.[9] Although a substantial tilt, this is a small fraction of the accommodation angle ($\theta_0 \simeq 110$ mrad) for the mismatch presented at these interfaces. This discrepancy will be discussed later.

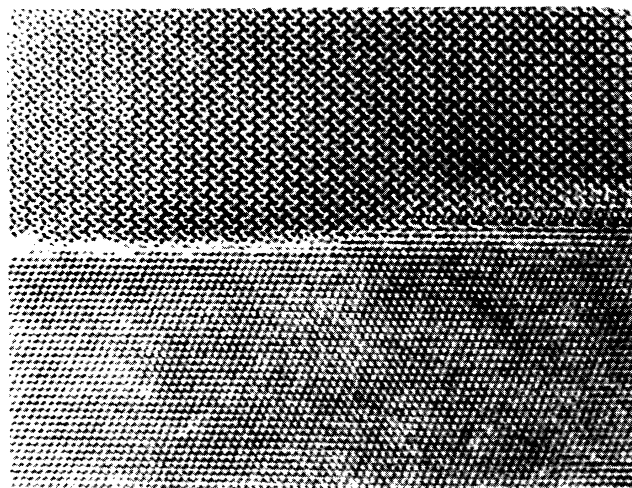

FIG. 2. A high-resolution transmission electron micrograph of an α-Si_3N_4(0001)/Si(111) interface formed *in situ* within a Si matrix. Although the field of view shows only 30 nm of interface, the total interface length was about 70 nm. The characteristic steps at the interface and the overall tilt of the two lattices can be clearly seen. Measurements indicate that the relative tilt of the coincident directions is roughly 5–10 mrad.

Asymmetric interfaces with tilts in the 1–10-mrad regime have also been observed in other heteroepitaxial structures have small amounts of mismatch. A particularly interesting example appears in a study by Wu of semicoherent Al_2Cu precipitates (with dimensions similar to the Si_3N_4 precipitates) grown *in situ* by annealing a random $AlCu_{0.08}$ alloy.[11] Analysis of high-resolution transmission electron micrograph images of the coherent interface again reveals a relative lattice tilt on the order of 10 mrad. In addition, similar amounts of interfacial tilt are also seen when mismatched III-V overlayers are grown on substrates tilted slightly from a low-index symmetry direction.[12,13] (The off-axis substrate breaks the symmetry presented by a flat surface.) The appearance of similar amounts of lattice tilt in chemically and physically distinct systems when the constraining symmetries are broken suggests that a general phenomenon is involved.

The principal driving force for formation of tilted interfaces is the reduction in the strain energy of the resulting structure. In the case of two adjoining crystalline half spaces, a stable coherent interface will only form at a minimum of the volumetric strain energy density

$$\Delta(\epsilon_0,\theta)=\frac{\mu(1+v)}{1+v}[\epsilon_0-a_1(1-\cos\theta)/a_0]^2, \quad (1)$$

where ϵ_0 is again the lattice mismatch, μ is the shear modulus, v is Poisson's ratio, θ is the interfacial tilt angle, and a_0 and a_1 are the unstrained lattice parameters of the two crystals. Note that the volumetric strain energies of the tilted coherent structure and the untilted but totally relaxed incoherent structure are both zero. This is an artifact of considering an interface between two infinite half spaces. In any finite system, the minimum in strain energy for the untilted relaxed structure is not the fully relaxed case. Instead, the residual strain decreases roughly as $\ln(h)/h$, where h is the overlayer thickness. In contrast, for the tilted coherent structure, the long-range strain field falls off exponentially with distance from the interface.[8] As a result, in real structures the untilted relaxed structure has much greater volumetric strain energy than the tilted coherent structure.

Consider the critical thickness for generation of misfit dislocations (or equivalently, extrinsic grain boundary dislocations) in a heterostructure where a lattice tilt θ is imposed between the two layers. The strain energy of the coherent structure is then the sum of the volumetric strain energy and the energy of the tilt boundary. In contrast, the strain energy of the incoherent structure is the sum of the tilt boundary energy and the energy of the misfit dislocation network. Since the tilt boundary energy appears in both cases, the equilibrium critical thickness[10] $h_c(\theta)$ for layers with an imposed lattice tilt θ is obtained by substitution of the effective interplanar mismatch $\epsilon(\theta)=\epsilon_0-a_1(1-\cos\theta)/a_0$ for the lattice mismatch ϵ_0. The critical thickness for coherent interfaces thus grows without bound as the interfacial tilt approaches θ_0.

In the examples described earlier, the observed tilt is much smaller than the accommodation angle θ_0. This occurs because an energy barrier separates the low-energy high-tilt structure from the higher-energy untilted structure (solid curve in Fig. 3). The source of this energy barrier is illustrated by considering a small-angle expansion of the energy of a coherent tilted structure. The volumetric strain energy reduces as θ^2, whereas the energy of the tilt boundary increases (in a dislocation-based model) roughly as θ. As a result, the strain energy increases in the early stages of precipitate tilt.

Given that the increase of energy of the tilt boundary dominates the energetics at small angle, why does the precipitate tilt at all? The answer is that the dislocation model for the tilt boundary breaks down when small tilts and finite structures are considered. In the dislocation model of grain boundaries, the distance between interfacial dislocations is $\simeq b/\theta$. If this distance is comparable to l, the linear extent of the precipitate surface, it is incorrect to describe the tilt boundary in terms of interfacial dislocations. Essentially, the precipitate can tilt a small amount without producing an interfacial dislocation. The tilt boundary energy is thus less than expected, and the reduction in volumetric strain energy will dominate for very small lattice tilt. As the tilt is further increased, the strain energy increases rapidly, producing a minimum in the precipitate energy at small, but finite, lattice tilt (dotted curve in Fig. 3). In practice, the minimum in energy should occur near the tilt at which

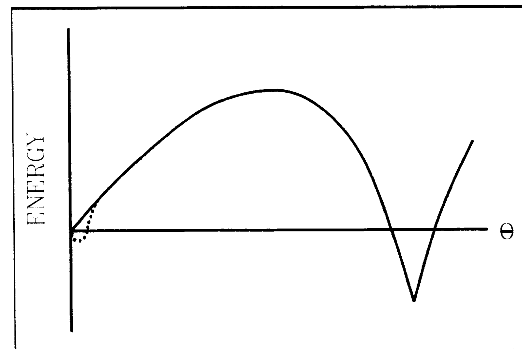

FIG. 3. A schematic representation of the energetics of tilt accommodation of mismatch. The solid curve represents the total strain energy for a structure having an asymmetric tilt boundary between two mismatched half spaces. Such a structure has a minimum in the strain energy at large tilt angles. The dotted curve portrays the total strain energy for a precipitate, in which the finite size greatly reduces the tilt boundary energy for small tilt angles. As a result, the strain energy can have a local minimum at small tilt separated from the global minimum by a large energy barrier.

the expected distance between interfacial dislocations is equal to the lateral extent of the precipitate. In the case of the Si_3N_4 precipitates, the minimum should occur near b/l. This amounts to a few milliradians, in agreement with observations.

Can growth of very thick mismatched overlayers with tilt near the accommodation angle θ_0 somehow be induced? If a tilted overlayer is to be grown on a substrate having a smaller lattice parameter, the strain-free tilt condition requires that the boundary be tilted with respect to the substrate lattice, but not with respect to the overlayer [Fig. 1(a)]. When the lattice mismatch is large (several percent), the transition between untilted growth on ledges and asymmetric tilted growth parallel to the interface requires only minor atomic relaxation near the interface. Strongly tilted substrates thus encourage growth of tilted overlayers. Another possibility is suggested by a recent study in which oriented ion bombardment during thin film deposition was shown to have a pronounced alignment effect on the crystallographic orientation of the growing film.[14] Accordingly, ion-controlled growth processes may be particularly useful for growth of tilted overlayers. In any case, this new mode of accommodation of lattice mismatch should substantially expand the class of material combinations available for practical applications. Efforts to harness this potential through control of lattice tilt thus present a high priority for further experimental studies.

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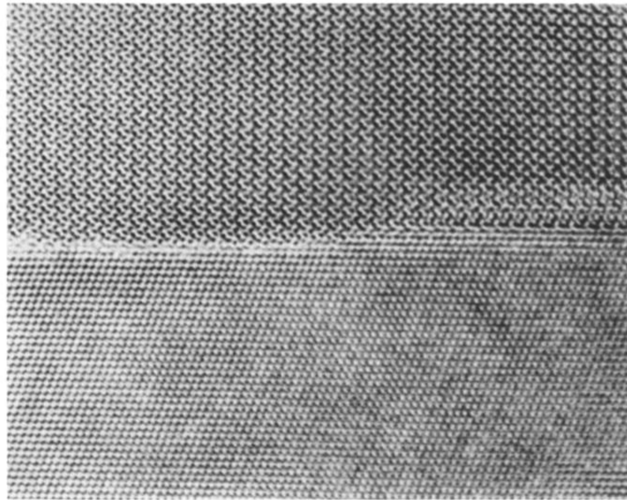

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