Growth and Dynamics of Metal Films

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Control of Variants in Heteroepitaxy by Substrate Miscut

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ABSTRACT

This paper discusses variants that occur in heteroepitaxy when the substrate possesses symmetries that are absent from the epilayer. Variants are enumerated in terms of 2-D symmetries of the substrate and epilayer, as they exist terminated at their interface. In this formulation, all possible cases can be presented in a single table. The role of miscut in controlling otherwise equal variants proportions is discussed with a view to eliminating unwanted variants and thereby improving the translational invariance of the materials. We summarize an experimental study of a (3m) symmetry epilayer growing on a (2mm) substrate, specifically Cu_3Au (111) grown by molecular beam epitaxy on Nb (110), for which the two variants predicted from symmetry are stacking twins. Miscuts of about 1° along the indicated azimuth are sufficient to eliminate all except ~ 0.1% of the less favored variant. This has interesting consequences in the context of the theory. A detailed understanding of the mechanisms for this example requires information about nanostructures that develop on the miscut Nb (011) surface. State-of-the-art information about novel substrate nanostructures, derived from scanning probe and low energy electron microscopies, is presented, and the prospects for a predictive science of variant control in heteroepitaxial growth are assessed.

1. INTRODUCTION

A problem arose in the 1980's when attempts were made to grow GaAs on Si or Ge in order to link optoelectronic materials with computer chips. For (100) Si or Ge substrate surface it was found that GaAs grew with two 'antiphase domains'. The diamond lattice of Si and Ge has two equivalent sites per fcc lattice point separated by [111]a/4, and the zincblende lattice has the same structure with Ga and As occupying these two sites per cell. The two antiphase arrangements have the Ga and As atoms interchanged. It was discovered (apparently without reference to theory) that miscut along [011] or [211] could be employed to eliminate one GaAs variant or the other on these (100) diamond-lattice substrates [1-3]. This is a valuable outcome because the presence of variants reduces the coherence of the crystal structure, and boundaries among variants scatter excitations and reduce carrier lifetimes, all generally undesirable results.

The larger context of this problem is that heteroepitaxy is vulnerable to variant creation as a matter of symmetry (reference 4 provides an introductory discussion). Variants of precipitates from the bulk have long been documented and explained [5]. It is easy to understand that precipitates with lower symmetry than the bulk can appear in several configurations which each bear an equivalent relationship to the more symmetric matrix in which they reside. The same holds true for an epilayer grown on a substrate. The case of GaAs grown on Ge is not the most primitive example because it is a glide operation, characteristic of nonsymmorphic crystals, that relates the two positions in the cell and hence the two variants (in this case antiphase domains). In other cases even Bravais lattices with one atom per site ('Bravais crystals') create variants, as

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in the Kurdjumov-Sachs example where one close-packed direction of an epilayer with a hexagonal surface plane aligns with either of the two [111] close packed directions of a bcc (110) substrate, to create two variants rotated from each other by 10.5° The present paper discusses the occurrence and elimination of variants in heteroepitaxy. From the perspective of theory the opportunities now appear clearly defined. However, the experimental flowering of this important topic remains in its early stages. There is a need for model cases, pursued to the point at which the both the symmetry and the detailed mechanisms are understood.

A theory of variant creation was formulated in the mid-1980's based on the theory of the crystallographic groups. It was formulated in terms of Shubnikov groups that describe the dichromatic complex of two interpenetrating bulk lattices [6]. The formulation employs 3-D crystallographic groups and is heavily mathematical. A simpler and more practical approach is now available. We have recently established that the content of the problem is entirely two dimensional, insofar as variant creation is concerned [7]. Consequently, all relevant information is contained in ten 2-D crystallographic groups, in place of the 230 3-D crystallographic groups together with the cuts of the two surface. As a result, the specification and prediction of variant behavior becomes much more accessible, and is now open to broad summary. This research provides the basis for understanding of observed variant suppression by miscut not only for GaAs but also for metallic compounds [8] high T_c superconductors [9], ferroelectric oxides [10] etc.

In this paper we first, in Section 2, review this new perspective on variant formation in heteroepitaxy, and in Section 3 then summarize the way miscut and multilevel surfaces can generally be employed to control variant proportions. Section 4 describes experiments in which Cu_3Au (111) is grown on Nb (110), and the proportions of two variants respectively stacked ABCA.... and ACBA..... examined as a function of miscut angle and azimuth with a view to confirming the symmetry predictions and exploring the microscopic mechanisms. Section 5 reports ongoing investigation of nanostructures on the Nb (110) surface that offer new opportunities to tailor the proportions in which variants occur.

2. ENUMERATION OF EPITAXIAL VARIANTS

Variants arise when the epilayer lacks symmetries that are present in the substrate; under these absent symmetry operations the epilayer transforms into distinguishable structures that nevertheless bear exactly equivalent relationships to the substrate lattice [4]. This basis for variant creation was recognized by Van Tenderloo and Amelynkx [5] for bulk variants in 3-D, and it is equally valid in 2-D for epitaxial variants.

Only ten different point symmetries are available to semi-infinite crystals that terminate parallel to a plane of the underlying Bravais lattice [10]. These are (1), (2), (3), (4) and (6), together with (m), (2mm), (3m), (4mm) and (6mm). The numbers signify the order of a rotational axis and the m denotes a mirror (objects with twofold rotational symmetry and a mirror necessarily possess two orthogonal mirrors); the axes and mirrors must be perpendicular to the surface plane. Accordingly, the numbers of variants that occur from point symmetry for all possible cases of heteroepitaxy take the values specified in Table 1. Because the different epilayer configurations are equivalent, the variants occur in equal proportions, when averaged over a sufficiently large substrate area. Each second row of the table gives the resulting global symmetry of the epilayer, which is the point symmetry of a diffraction pattern that senses all variants equally (it is the union of the epilayer and substrate symmetries). The experiments

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described in Section 4 concern fcc (111), with (3m) symmetry, grown on bcc (110), with (2mm) symmetry, so the number of variants from Table 1 is 2. These turn out to be the stacking twins mentioned above.

A number of additional matters warrant attention. Because of space limitations the reader should consult the original work for details [7]; brief comments must suffice here. Specifically, variants that differ only by a translation vector ('translational variants') may, in addition be created by a translational symmetry of the substrate that the epilayer lacks or, on multilevel surfaces, because the substrate and epilayer have different interatomic spacings (which in addition creates inhomogeneous strain in the epilayer near interfacial steps). In some circumstances translational and point symmetry operations are coupled, in which case point symmetry labels are to be preferred because strains from interfacial steps can eventually

E \ S	1	m	2	2mm	3	3m	4	4mm	6	6mm
1	1 (1)	2 (m)	2 (2)	4 (2mm)	3 3)	6 (3m)	4 (4)	8 (4mm)	6 (6)	12 (6mm)
m	1 (m)	1 (m)	2 (2mm)	2 (2mm)	3 (3m)	3 (3m)	4 (4mm)	4 (4mm)	6 (6mm)	6 6mm)
2	1 (2)	2 (2mm)	1 (2)	2 (2mm)	3 (6)	6 (6mm)	2 (4)	4 (4mm)	3 (6)	6 (6mm)
2mm	1 (2mm)	1 (2mm)	1 (2mm)	1 (2mm)	3 (6mm)	3 (6mm)	2 (4mm)	2 (4mm)	3 (6mm)	3 (6mm)
3	1 (3)	2 (3m)	2 (6)	4 (6mm)	1 (3)	2 (3m)	4 (12)	8 (12mm)	2 (6)	4 (6mm)
3m	1 (3m)	1 (3m)	2 (6mm)	2 (6mm)	1 (3m)	1 (3m)	4 (12mm)	4 (12mm)	2 (6mm)	2 (6mm)
4	1 (4)	2 (4mm)	1 (4)	2 (4mm)	3 (12)	6 (12mm)	1 (4)	2 (4mm)	3 (12)	6 (12mm)
4mm	1 (4mm)	1 (4mm)	1 (4mm)	1 (4mm)	3 (12mm)	3 (12mm)	1 (4mm)	1 (4mm)	3 (12mm)	3 (12mm)
6	1 (6)	2 (6mm)	1 (6)	2 (6mm)	1 (6)	2 (6mm)	2 (12)	4 (12mm)	1 (6)	2 (6mm)
6mm	1 (6mm)	1 (6mm)	1 (6mm)	1 (6mm)	1 (6mm)	1 (6mm)	2 (12mm)	2 (12mm)	1 (6mm)	1 (6mm)

***Table I.** The number of variants formed in epitaxial growth, listed by symmetry of the substrate, S, and epilayer, E, and with the global symmetry given in parenthesis. The results are valid for substrates that are Bravais lattices, and for single terraces of any other substrates. For multilevel surfaces, the results hold provided that screw axes normal to the surface are treated as simple rotation axes, and glide planes that contain the surface normal are treated as simple mirrors. For the 25 cases in which both the substrate and epilayer symmetries include mirrors it has been assumed that these mirrors are parallel. If they are not parallel the number of variants is doubled, but the global symmetry is not changed. Screw axes that are perpendicular to the surface can alter the global symmetry .*

blur translational characteristics. In lattices with a basis, variants can be created by screw axes and glide operations associated with the symmetries of the basis. Indeed, the GaAs variants on Ge, mentioned above, derive from the glide symmetry that constrains the two atoms per cell of the diamond lattice.

Lattice strain is of special importance for epitaxial crystals. Interfacial stresses cause thin films to be strained, but stresses that remain constant over the entire interface cause the film to adopt a strain that is uniform through the entire film thickness, as may readily be established from the equations of elastic equilibrium [11] (or more generally by lattice statics for a discrete crystal lattice). It is an important point that, while spatially uniform, the epitaxial strain is generally anisotropic, and can change the symmetry of the epitaxial material from that of the bulk. For example, a cubic crystal generally becomes tetragonal on a substrate which has a square surface net, or orthorhombic as an epilayer which has a tetragonal surface net.

3. USE OF MISCUT TO CONTROL VARIANT POPULATIONS.

All variants must occur equally on an unbiased substrate surface, since by symmetry they are equivalent [4]. Miscut can be employed to break the symmetry, and so favor particular variants at the expense of others. In practice a miscut of 1° has proved sufficient to saturate the nucleation process and eliminate almost all unwanted variants [8]. Of interest are the symmetry of miscut effects, the physical mechanisms by which the miscut changes variant populations and the way the resulting variant populations depend on the azimuth of the miscut. The main point is that miscut can be employed to break a substrate symmetry that the epilayer lacks, and thus eliminate the undesirable equivalence of the variants that arise from this substrate symmetry.

(a) Symmetry of variant repopulation. We can represent miscut through a small angle by a vector $\mathbf{m} = \theta\,\eta$, in which θ is the size of the miscut and the vector η its azimuth. Its effect is to introduce a bias into the distribution of step edges or step bunches on the surface. This in turn biases the efficiencies with which variants nucleate and grow, and so changes the otherwise equal variant populations. The effects can be understood by recognizing that while variants must nucleate and grow equivalently on a flat terrace, they do so unequally at steps edges where, first, they are offered a larger coordination, and second, the terrace symmetry is broken. The sketch in Fig 1(a) indicates for a 1-D example how particular variants may occur preferentially at alternative types of step. Given that widely spaced steps act independently, the bias on variant populations in this limit must be linear in the angle θ. We write the fraction of α from n variants as $n^{-1} + C\theta\, f_\alpha(\phi)$, with ϕ the angle between η and a chosen zero, and C a constant.

Our concern is with the variation of f_α with ϕ; it is fixed by symmetry to the following extent. First, any point symmetries of the substrate that are shared by the epilayer are symmetries of the entire system and are shared by $f_\alpha(\phi)$. Second, symmetry elements of the substrate that are not shared by the epilayer are responsible for the variants and may be used to label the variants to which they give rise. Then variants created by an uncancelled n-fold rotation axis of the substrate must exhibit equivalent behaviors. Thus only one is independent, say $f_0(\phi)$, while the remainder follow from $f_p(\phi - 2\pi p/n) = f_0(\phi)$. Similarly a mirror in the substrate not present in the epilayer creates two variants which have equal populations when the miscut lies in the mirror, and which are otherwise related by $f_\alpha(\phi) = f_{\alpha'}(-\phi)$, where ϕ is now measured from the mirror.

These symmetry-constraints on variant populations are not easily visualized. Moreover, the results in particular cases are sensitive to details of nucleation and growth. To clarify the behavior we present the results of model calculations for growth under conditions where nucleation on steps competes with nucleation on terraces. The substrate is taken to have (2mm)

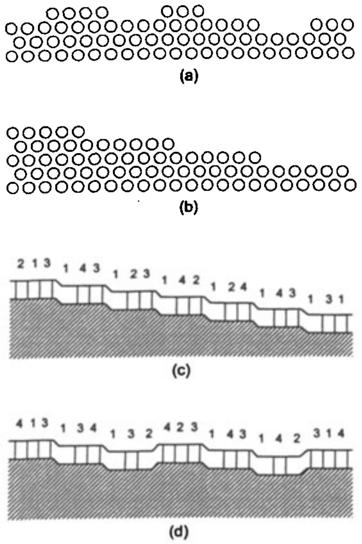

Figure 1. (a) rough surface; (b) miscut surface; (c) variants on miscut surface showing preference for variant 1 at the step; and variants on a surface which is both rough and miscut.

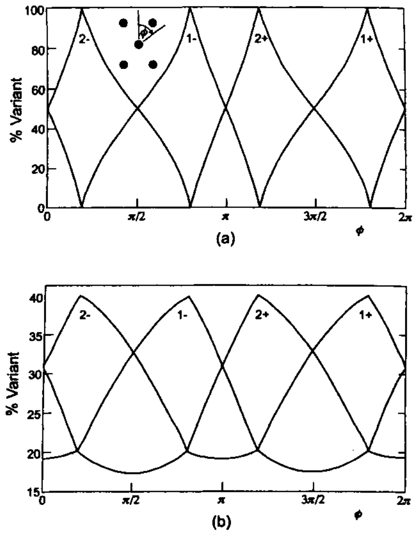

Figure 2. The dependence of variant proportions on the azimuth of miscut for the model calculation described in the text.

symmetry and the epilayer no symmetry, so that there are four variants in two pairs related by the substrate mirrors. The detailed behavior depends on the growth model. Here we assign vectors $\mathbf{a_1}$, $\mathbf{a_2}$ to the net of surface atoms, and postulate that each variant occurs only at one type of step, variants ±1 at ±$\mathbf{a_2}$ (ie the two senses of steps with edges parallel to $\mathbf{a_2}$), and similarly variants ±2 at ±$\mathbf{a_1}$. The average step orientation due to miscut is along $\boldsymbol{l} = \eta \times \mathbf{n}$ with $\mathbf{n}$ the terrace normal. We assume that they break into facets oriented down the surface gradient, parallel to $\mathbf{a_1}$ and $\mathbf{a_2}$. This completely specifies the variant population when each facet creates only one variant. Figure 2 presents the results of completed calculations for two cases in which (I) terrace nucleation is negligible, and (II), the step nucleation is a small perturbation on dominant terrace nucleation. In (I) each variant is seen to occur uniquely ($f = 1$) for the single orientation in which the miscut creates that step alone, and its proportion decreases from geometrical causes to zero for a range π of miscut orientations ϕ for which the projection of the step normal on η is negative. Rotational variants are seen in the results to possess equivalent angular dependences, merely rotated by π. The proportions of +1 and -2 are images in one mirror, as are -1 and +2 in the other mirror. The same symmetry but with generally weaker variation occurs in case (II), when the step nucleation competes with terrace nucleation. Overall, Figure 2 shows that strong variations of $f(\phi)$ with ϕ occur for a particular case, and this is

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especially striking when terrace nucleation is comparatively weak. In no real case has the specific form of f(ϕ) yet been determined experimentally.

(b) Substrates with a basis. The comments here relate to common lattices with two atoms per cell, specifically hcp, diamond, rocksalt, zincblende CsCl and the WC lattice (hcp but with two inequivalent atoms per cell). We are interested in the degree to which miscut, or multilevel surface structure more generally, may be employed to discriminate among variants that would otherwise occur with equal populations.

The crystal planes of lattices with two atoms per Bravais cell either all contain whole formula units, or else the two sites of the cell occupy alternating successive planes. Formula unit planes are generally to be avoided as they can generate added variants associated with the translation vector between successive terraces. When the two atoms of the basis are identical, even when the planes they occupy alternate, they may still remain chemically equivalent if the sites are related by a glide operation. This introduces a further opportunity for the formation of variants that are interrelated by the glide operation. It can be shown that glide-related variants

substrate	formula units	basis symmetry	active surfaces
diamond	{110}{130}{211} {330}{332}	{100}{110}{120} {230}	{111}{113}{122} {133}
hcp	$\{11\bar{2}0\}$ $\{11\bar{2}2\}$	{0001} $\{11\bar{2}0\}$	$\{1\bar{1}00\}$ $\{1\bar{1}01\}$
	$\{11\bar{2}2\}$	$\{11\bar{2}1\}$ $\{11\bar{2}2\}$	$\{\bar{1}02\}$
CsCl	{110}{211}		{100}{111}{210}
rocksalt	{100}{110}{112} {123}{221}{223}		{111}{113}{133}
zincblende	{110}{310}{211} {330}{332}		{100}{210}{111} {113}{221}{230}

Table II. *Low-index planes of diatomic crystals that contain formula units (column 1) that have normals in a glide plane (column 2), and remaining planes that yield generally inequivalent populations of basis-related variants (column 3).*

remain equivalent whenever the terrace normal lies in a glide plane. The case of GaAs on Ge discussed above for the (100) surface provides examples of this problem. Specifically, two variants are created equivalently whenever the surface normal is contained in the {001} glide plane, and this equivalence may purposefully be eliminated by a miscut that takes the surface normal out of the glide plane (eg along [011] for (100)). When the two atoms per substrate cell are chemically distinct there still remains the problem of formula-unit planes. Table 2 summarizes for the six diatomic substrate lattices those low-index crystal planes that are active in rendering basis-derived variants chemically inequivalent. The conditions mentioned above for Bravais crystals still determine the way miscuts control variant populations on a single terrace.

4. EXPERIMENTAL STUDIES OF Cu_3Au (111) GROWN ON Nb (011)

The growth of Cu_3Au twin variants on Nb (011) has been studied experimentally [8] to yield information relevant to the conditions under which variants form. In equilibrium at the growth temperature of ~300°C, Cu_3Au takes the ordered Lw_2 structure with a fcc array of atoms in which Au atoms occupy only the cube corner sites of the conventional unit cell. It is observed [8] that, initially, the as-grown (111)-oriented alloy is almost completely disordered, presumably because the growth process, at ~ 5 monolayers per minute, allows insufficient time for the diffusion required by ordering; hours of annealing below the ordering temperature of 390°C are subsequently needed to produce the fully ordered configuration.

The (2mm) symmetry provided by the Nb (110) terrace affords no template that can distinguish between the alternative stackings of the fcc disordered alloy. Given an A plane deposited on the Nb surface, the ABCA.. and ACBA... stackings of close packed planes are mirror images (twins) in the Nb (100) plane, and consequently occur as two variants with equal populations. This conforms with the symmetry prediction in Table 1 for two variants of (3m) Cu_3Au (111) grown on (2mm) Nb (110). The incoherent twins do not grow out under prolonged annealing. Consequently the observed twin structures result from symmetry of the initial disordered fcc alloy, rather than the final ordered structure, and will therefore be discussed here in terms of the fcc structure. Figure 3(a) shows by sketches the succession of planes in the stacking of the two twins, with close packed layers shifted each layer by ± [112]/6 in the two cases (arrows). The Nb (110) surface on which these structures grow is sketched in Figure 3(b) in the correct orientation relative to the twins. By means of x-ray diffraction it is easy to determine which twin a structure comprises. The full (large) and empty (small) circles in Figure 4 indicate the locations of diffraction wavevectors in reciprocal space for the respective twins. The two sets of spots are mirror images in the (112) planes.

In general the x-ray beam overlaps many domains of each twin, with the result that their diffraction patterns can both be detected. The relative integrated intensities of the two sets of spots then measures the relative volumes of two twins that have grown. The experimental results for the intensity ratio [8] are shown as a function of miscut magnitude and azimuth,

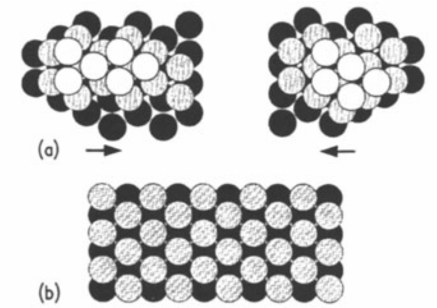


Figure 3. *(a) Succession of close packed planes in the two twins, distinguished by opposite displacements along [112]; and (b) the Nb (110) substrate stacking.*

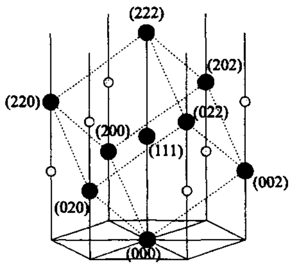
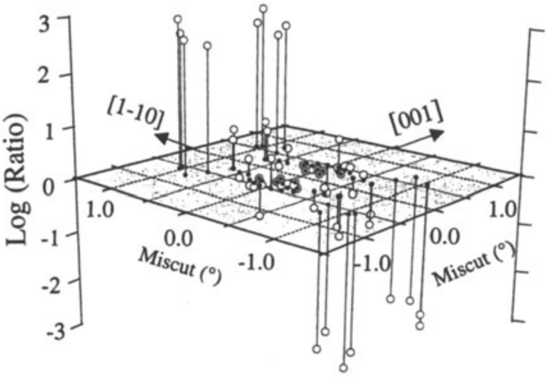


Figure 4. *The diffraction spots for the two variants are shown*

and on a logarithmic scale, in Figure 5. These are mainly data taken from samples with random miscuts with both the miscut and the intensity ratio determined after the growth was completed. In all, 15 samples were measured. In Figure 5, the intensity ratio for each sample is plotted four times, using the presumed even symmetry of relative intensities along [001] and presumed symmetry with the reciprocal for miscuts along [1$\bar{1}$0]. The data in Figure 5 show considerable scatter but are certainly consistent with the expected variations with ϕ, based on the substrate and epilayer symmetries.

Figure 5. The logarithm of the Cu3Au twin ratio shown as a function of the surface miscut vector.



It is most interesting, in Figure 5, that the expected range of small miscuts, for which the variant ratio changes linearly with miscut angle, is <u>not</u> detected in practice. Instead, the ratio appears to remain near unity for all miscuts less than about 0.5°. For larger miscuts the ratio increases rapidly, until at ~1° the less favored variant is almost completely eliminated. This may perhaps be consistent with the ideas sketched in Figure 1. It is necessary to believe that the combination of roughness and miscut realized on the substrate as the miscut is increased must eliminate almost all steps that oppose that miscut. A 1° miscut creates steps roughly every 10^2 A. It is hard to believe that this is 10^{-2} of the length scale of the roughness, in order to achieve a ratio 10^2 of the two signs of step edge. Therefore one infers that the introduction of biased substrate steps from miscut actually eliminates the background of opposing steps expected from roughness. This interpretation seems very reasonable if opposing steps anihilate during the pre-annealing of the substrate.

5. NANOSTRUCTURES ON THE MBE-GROWN Nb (110) SURFACE.

While the preceding discussion of miscut has been phrased here in terms of Nb surface steps, evidence has accrued that nanostructures with important physical attributes either occur on the Nb free surface during growth by molecular beam epitaxy [13], or may be induced by post-growth processing of the MBE-grown material [14]. The opportunity arises to tailor nanostructures for use in variant suppression. This is a field that as yet scarcely exists, but there seems little doubt that its importance will increase as methods are perfected to manipulate surface structures and selectively influence the growth of variants. Here we summarize information that pertains to the Nb (110) surface alone.