Cambridge University Press
978-1-107-40576-9 - Materials Research Society Symposia Proceedings: Volume 56: Layered Structures and Epitaxy
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PART I

Epitaxial Growth of Semiconductors

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INTERFACIAL DEFECTS AND EPITAXY

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ABSTRACT

It is shown that interfacial defects are characterised by combinations of symmetry operations, one from each of the adjacent crystals. This approach demonstrates that the variety of possible interfacial defects is broader than had been previously recognised, and includes disclinations and dispirations in addition to dislocations. The condition of the initial substrate surface is shown to have a very important influence on the character and stability of interfacial defects.

INTRODUCTION

The quality of epitaxial layers is profoundly influenced by the presence of defects in the interface. Appreciation of this fact has encouraged a great deal of experimental and theoretical research. In particular, the role of arrays of interfacial dislocations in the accommodation of 'lattice mismatch' in epitaxial systems is well understood [1]. However, crystals may exhibit more than merely translation symmetry, and, in order to appreciate the full range of possible interfacial defects, it is necessary to consider the complete spatial symmetry of both the adjacent crystals. Recently, based on theoretical crystallographic methods for treating the total symmetry of bicrystals [2,3], a theory of interfacial defects has been presented [4]. The objective of the present paper is to highlight the key points of this theory, and to discuss its implications regarding epitaxial systems. This paper is therefore written from a tutorial point of view, and readers interested in a comprehensive treatment of interfacial defects are referred to the original papers.

CHARACTERISATION OF DEFECTS IN SINGLE CRYSTALS

An important feature of the recently published theory of interfacial defects is the characterisation of defects without using the conventional method of constructing a circuit around the defect and subsequently mapping this circuit onto perfect crystal. The conventional methods are very useful for characterising observed defects, but are not necessary in order to predict the defects which can exist in a given crystal structure. The geometrical character (i.e. the Burgers vector of a dislocation for example) of admissible defects depends only on the symmetry exhibited by the perfect crystal, and we consider below the characterisation of line-defects in single crystals.

Line-defects can be introduced into a crystal by the Volterra process [5], i.e. a cut is made in the crystal and the two surfaces are rewelded together after an appropriate displacement or rotation, material being removed or added as necessary. The two surfaces can only be joined together without introducing a planar defect into the crystal if the operation which brings the two surfaces together is a symmetry operation of the crystal. Thus, a line-defect is geometrically characterised by the operation required to bring the two Volterra surfaces together. The defect is a dislocation, disclination or dispiration if the operation is a translation, proper rotation or screw-rotation respectively. In the case of dislocations the translation characterising the defect is, of course, equal to the Burgers vector. In

Mat. Res. Soc. Symp. Proc. Vol. 56. © 1986 Materials Research Society

principle, one type of admissible line-defect corresponds to each type of proper symmetry operation (i.e. translation, rotation or screw-rotation) exhibited by a crystal. However, in the case of three-dimensional crystals, the elastic energy of line-defects is relatively modest only in the case of dislocations with small magnitude Burgers vectors.

In addition to line-defects it is important to consider planar-defects (domain boundaries) in crystals which exhibit lower symmetry than the lattices on which they are based. Such defects cannot always be introduced by a Volterra process, but they can be characterised by symmetry operations. However, these symmetry operations are not exhibited by the perfect crystal structure, but correspond to the parent crystal structure from which the structure in question can be considered to have been derived. As an example we consider the sphalerite structure which can be regarded as being derived from the diamond structure. The projection along [001] of the diamond structure is shown in fig. 1. The circular and square sites can be regarded as two fcc atomic arrays displaced with respect to each other by $\frac{1}{4}[111]$. These two sets of sites are related to each other by twenty four symmetry operations, for example one of these is the diamond-mirror-glide plane 'd' indicated in the figure. Now, in the sphalerite structure the two sets of sites are occupied by different atomic species, and hence the twenty four symmetry operations mentioned above are supressed. The effect of operating any one of these operations on a crystal of sphalerite is to interchange the atomic species, i.e. to create an antisite crystal. When such antisite structures coexist in a crystal they are separated by a domain boundary as illustrated in fig. 6. The domain boundary is geometrically characterised by any one of the symmetry operations which inter-relate the two domains, and we refer to these as exchange operations. In the sphalerite structure we refer to such domains as inversion domains because the inversion operation about the point $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ is also one of the twenty four exchange operations; the name antiphase domains is inappropriate in this case because it is not possible to relate the domains by a displacement.

We have shown that line-defects and domain boundaries in single crystals can be characterised conveniently by symmetry operations. We note that this method of characterisation is independent of the line direction of a line-defect (i.e. the screw or edge nature of a dislocation for example is not specified) and the orientation of the plane of a domain boundary. In addition, this approach emphasises the fact that the character of admissible defects, which are discontinuities of the crystal order, is determined by the order (symmetry) exhibited by the perfect crystal (or parent crystal in the case of domain boundaries).

INTERFACIAL DEFECTS

We consider an epitaxial interface to be created by bringing together the substrate and overlayer crystals as shown schematically in fig. 2. The two crystals have the required structures and relative orientation and are brought together so that previously prepared surfaces are juxtaposed. When the two crystals bond together relaxation occurs in the interfacial region. In general we do not know the details of such relaxation unless sophisticated experimental measurements can be made or the interface can be modelled using advanced simulation techniques. Later we will show that relaxations which break symmetry can lead to particular types of interfacial defects, and the character of these can be obtained if the nature of the relaxation is known. For the moment we assume that no such relaxations occur, and it is then readily possible to predict the character of admissible interfacial defects.

Because the component crystals exhibit symmetry it is possible to expose new surfaces on both the substrate and overlayer which are crystallographically equivalent to the initial ones. Let the symmetry operations of

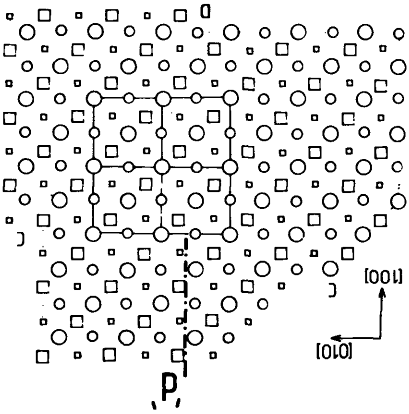

Fig. 1. [001] projection of the diamond structure; 'd' diamond-mirror-glide plane, C complete surface step D demi-step.

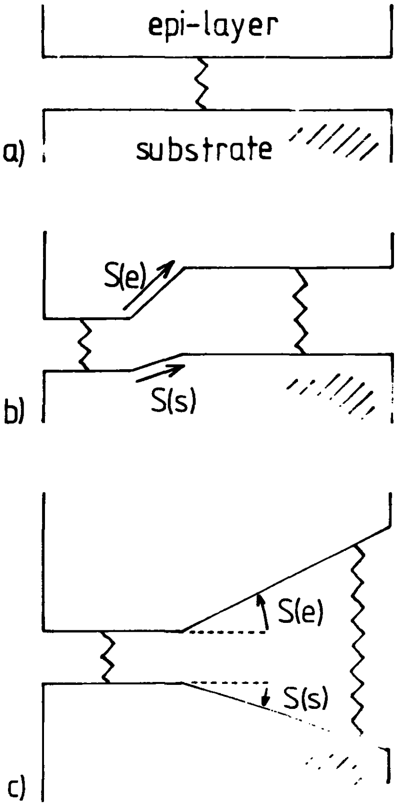

Fig. 2. Schematic illustration of discontinuities in an epitaxial interface. (a) initial surfaces before bonding, and (b) and (c) initial and new surfaces related by translation and rotation symmetry respectively.

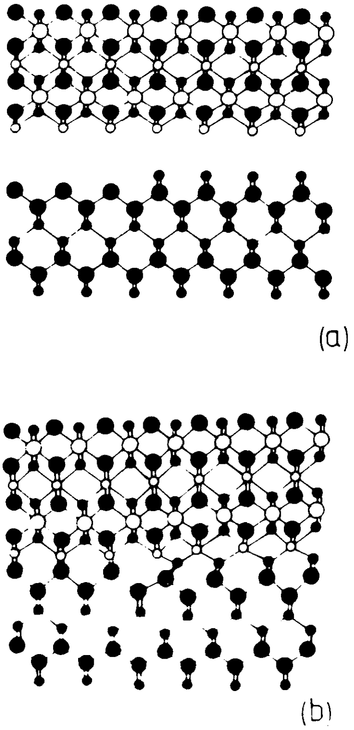

Fig. 3. Schematic illustration of the formation of $\frac{1}{4}\langle 111\rangle$ dislocation in $NiSi_2$:(001) Si. (a) initial unstepped $NiSi_2$ and demi-stepped Si surfaces, (b) interfacial dislocation after bonding.

the substrate be designated S(s) and those of the epitaxial layer be S(e), and let the downward pointing unit normals to the initial surfaces be designated $\underline{n}(s)$ and $\underline{n}(e)$. It follows that new equivalent surfaces having normals S(s) $\underline{n}(s)$ and S(e) $\underline{n}(e)$ can be created on the substrate and epitaxial crystals respectively. Fig. 2(b) shows schematically the case where S(s) and S(e) are both translation operations, so that the new and initial surfaces have the same structure and orientation in space but are separated by a surface step. In fig. 2(c) the new surfaces are related to the initial ones by proper rotations.

Now bring the two initial surfaces together and allow them to bond, and, also, force the new surfaces together. Since the two new surfaces are equivalent to the initial ones they may bond together to form an interfacial structure which is crystallographically equivalent to the initial one. These two interfacial regions would then be separated by a discontinuity characterised by the operation required to bring the two new surfaces together. This latter operation is given by the product

$$S(e)\ S(s)^{-1} \qquad (1)$$

and corresponds to an admissible interfacial line-defect if it is proper. In other words, admissible interfacial defects are characterised by combinations of symmetry operations, one from each of the adjacent crystals. The defect is an interfacial dislocation, disclination or dispiration when the compound operation $S(e)\ S(s)^{-1}$ is a pure translation, a proper rotation, or combination respectively. We note that the compound operation must be proper, but the component operations can be either both proper or both improper.

The arguments presented above can be extended to the case where the substrate and/or the overlayer are nonholosymmetric and can hence exhibit domain structures. In Such crystals equivalent surfaces can be exposed as described above, but in addition, the initial surface is related by exchange operations to equivalent new surfaces in other domains. The topological feature separating such initial and new surfaces (step, facet junction or combination) therefore delineates the emergence of a domain boundary from the bulk onto the surface. Thus, exchange operations of either the substrate or epitaxial crystal (or both) can be substituted into expression (1), and, provided the compound operation is proper, the corresponding line-defect is admissible and delineates the intersection with the interface of a domain boundary in one (or both) of the adjacent crystals.

MATRIX FORMULATION OF SYMMETRY OPERATIONS

The most convenient way to express relation (1) is to represent the symmetry operations using matrix formulation. As explained in the introduction to the International Tables for Crystallography [6], a translation, $\underline{\tau}$, is expressed as $[E/\underline{\tau}]$ where E represents the identity matrix. Point symmetry operations are expressed as $[D/\underline{\alpha}]$ where the matrix D represents rotation, inversion, roto-inversion or reflection, and $\underline{\alpha}$ is the supplementary displacement associated with the operation. In the case of symmorphic crystals, for which no screw-axes or mirror-glide planes are included in the spacegroup, all the point symmetry operations exhibited by the crystal intersect at a common point which can be regarded as a lattice point. It is then convenient to take this point as the chosen origin, and the supplementary displacements, $\underline{\alpha}$, will then all be zero. On the other hand, in the case of nonsymmorphic crystals, some of the supplementary displacements will not have zero magnitude. In such cases $\underline{\alpha}$ includes not only any translation inherent in the operation in question, but also a further component which arises if the operation does not act through the chosen origin [4,6].

Generally it is expedient to use the coordinate frame of one of the crystals. If the epitaxial crystal's frame is used for example, expression (1) becomes

$$S(e)\ T\ S(s)^{-1}\ T^{-1} \qquad (2)$$

where T is the transformation matrix relating the coordinate frames of the two crystals.

INTERFACIAL DISLOCATIONS

According to expression (1) interfacial dislocations can arise in two different ways. Firstly, they arise when both the component symmetry operations are translations, i.e. $[E/\underline{\tau}(s)]$ and $[E/\underline{\tau}(e)]$, as depicted schematically in fig. 2(b). This case includes the familiar instance of the misfit dislocation where the Burgers vector is that of a crystal dislocation of one of the component crystals. For example, S(s) may be the identity operation [E/0], and S(e) may be $[E/\underline{\tau}(e)]$. If $\underline{\tau}(e)$ is parallel to the surface (i.e. $\underline{n}(e).\underline{\tau}(e) = 0$) no topological features are present on the substrate and epitaxial layer surface before bonding, and the resulting dislocation accommodates lattice misfit efficiently. On the other hand, consider the case where the substrate surface exhibits a step, i.e. $S(s) = [E/\underline{\tau}(s)]$ and the step height is given by $\underline{n}(s).\underline{\tau}(s)$. The epitaxial crystal can accommodate such a surface step by exhibiting a complementary step. However, if $\underline{\tau}(e) \neq \underline{\tau}(s)$ (when expressed in the same coordinate system) expression (1) shows that interfacial dislocation character, with Burgers vector equal to $\underline{\tau}(e)-\underline{\tau}(s)$, is developed after bonding. Such a dislocation would have a component perpendicular to the interface equal to the difference of the surface step heights, i.e. $\underline{n}.(\underline{\tau}(e)-\underline{\tau}(s))$.

The type of interfacial dislocation described above may be important in epitaxial technology. The discussion above shows that surface features on the substrate, such as steps, must be accommodated by the epi-layer and these features may develop dislocation character. Thus, arrays of substrate surface steps, which are sometimes intentionally introduced in order to facilitate nucleation of the epi-layer, may be transformed into interfacial dislocation arrays. The component of the Burgers vector of each such dislocation parallel to the interface can contribute to the accommodation of misfit. On the other hand, the perpendicular components can act like a low angle tilt boundary (if the initial array of substrate steps is regular) thereby modifying the orientation of the overlayer. This effect has been found recently [7] in a study of very accurate relative orientation measurements of silicon-on-sapphire. The substrate orientation was slightly off $(01\bar{1}2)$ and was assumed to be stepped, and the average inter step spacing, x, was determined. The angle of tilt,δ , between the (001) silicon planes and the $(01\bar{1}2)$ sapphire planes could then be predicted assuming that the array of surface steps exhibits dislocation character after deposition. As explained above the perpendicular component of the Burgers vector, $\underline{b}'$, is equal to $\underline{n}.(\underline{\tau}(e)-\underline{\tau}(s))$, and, assuming $\underline{\tau}(e)$ and $\underline{\tau}(s)$ to be primitive translation vectors, excellent agreement was obtained between the calculated values of $\delta = b'/_x$ and the observed values. Now it is known that the strain field of a low angle tilt boundary extends to a distance from the boundary approximately equal to the dislocation spacing [8]. Thus, regular arrays of substrate surface steps may not lead to long range strain fields in epitaxial films. However, if the substrate surface is roughened, exhibiting 'hill and valley' features for example, long range strains may be produced following deposition.

Another type of interfacial dislocation can arise when one or both of the crystals is non-symmorphic and where point symmetry operations are oriented parallel. For example, consider a substrate crystal such as (001) silicon;

such surfaces can exhibit demi-steps [9] as illustrated schematically in fig. 2 by the feature D. The two surfaces separated by such a demi-step are related by, for example, the 'd' mirror-glide plane perpendicular to the surface. The matrix formulation for this operation, choosing an atomic site as origin, is $[m(s)/\underline{\alpha}(s)]$, where m represents reflection and $\underline{\alpha} = \frac{1}{4}[111]$ for the diamond structure. It can be seen that the height of the demi-step is $\underline{n}(s).\underline{\alpha}(s) = \frac{1}{4}[001]$. Now imagine that an epitaxial layer having the fluorite structure is deposited and has the same orientation as the substrate. The complementary surface of the fluorite exhibits ordinary mirror symmetry perpendicular to the surface. This operation is represented as $[m(e)/0]$, and hence no demi-steps can exist on such surfaces. Substituting into expression (1) we obtain the compound operation $[E/-\underline{\alpha}(s)]$, i.e. a dislocation with Burgers vector equal to $-\alpha(s)$. The formation of such a defect is illustrated schematically in fig. 3(a) and (b) before and after bonding respectively. Unit cells of the fluorite and silicon structures are illustrated in fig. 4(a) and (b) projected along [001]. The origin of $\frac{1}{4}\langle 111\rangle$ interfacial dislocations can be regarded as being due to two alternative but equivalent sites for metal atoms, such as A, to bond to Si. For (001) substrates the interfacial energy will be identical whether A bonds to Si atom B or C since these two possible structures are related by symmetry. Thus, $\frac{1}{4}\langle 111\rangle$ dislocations separate crystallographically equivalent regions of interface. Such dislocations can only exist in interfaces with particular orientations, because the surface structures surrounding atoms B and C are only related by symmetry for particular surfaces. These latter surfaces are those for which the operations $[D(s)/\underline{\alpha}(s)]$, which relate atoms B and C, also leave the orientation of the surface normal, $\underline{n}(s)$, invariant. Thus, in the case of diamond structure substrates, where A and B type sites are related by the twenty four operations for which $\underline{\alpha} = \frac{1}{4}[111]$, the set of surface normals has been shown to be {hk0}, i.e. those orientations where at least one Miller index is zero. These theoretical predictions are in complete agreement with experimental observations using transmission electron microscopy of $NiSi_2$:Si interfaces [9].

In the case of the $NiSi_2$Si interfaces discussed above the lattice parameters of the two crystals are virtually identical. The observation of defects in such interfaces therefore emphasises the point that matching the lattices of substrate and epitaxial crystals is a necessary but not sufficient criterion for avoiding interfacial dislocations. Even where lattices are exactly matched, other differences of symmetry between the adjacent crystals can lead to dislocations. Another example where similar defects can arise is silicon-on-sapphire; in this case a 'c' mirror-glide plane $(2\bar{1}\bar{1}0)$ of the substrate is parallel to a diamond mirror-glide plane (010) of the overlayer, as indicated in figure 4(b) and (c). The matrix formulation of these operations is $[m(e)/\underline{\alpha}(e)]$ for the silicon, where $\underline{\alpha}(e) = \frac{1}{4}[111]$, and $[m(s)/\underline{\beta}(s)]$ for the sapphire where $\underline{\beta}$ can be expressed as $\frac{1}{3}[2\bar{2}01]$. Substituting into expression (1) the compound operation $[E/\underline{\alpha}(e) - \underline{\beta}(s)]$ (where we take $\underline{\alpha}(e)$ and $\underline{\beta}(s)$ to be expressed in the same coordinate system) is obtained, characterising a dislocation with Burgers vector $\underline{\alpha}(e) - \underline{\beta}(s)$. Such dislocations can exist on the $(01\bar{1}2)$ interface plane because the 'c' mirror-glide plane leaves the orientation of the normal to this plane invariant. In addition, similarly to the case of fluorite: silicon interfaces, the two regions of interface separated by such dislocations are crystallographically equivalent and correspond in one case to Si atom B bonding to Al atom D, and in the other to C bonding to E (fig. 4(b) and (c)).

INTERFACIAL DISCLINATIONS

Interfacial disclinations can arise when S(e) and S(s) are both proper or improper rotations, or reflections. In particular, the rotation characterising the resulting disclination can have small angular magnitude

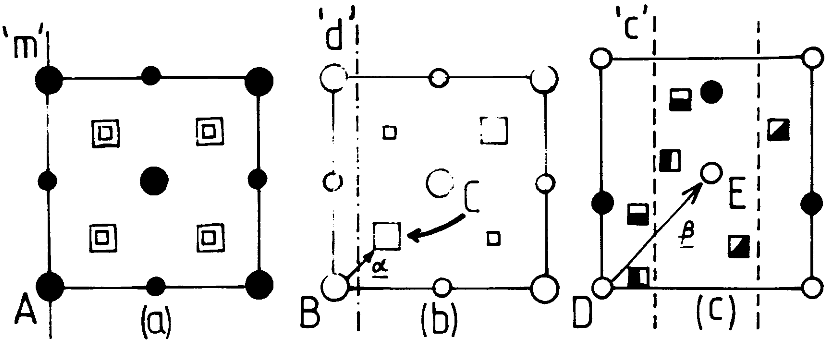

Fig. 4. Schematic projections of unit cells, (a) fluorite (001), (b) diamond (001), (c) sapphire (01$\bar{1}$2). The orientation and location of mirror and mirror-glide planes is shown.

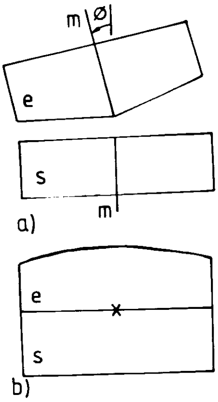

Fig. 5. Schematic illustration of an interfacial disclination arising because of a small misorientation, ∅, of mirror planes; (a) before bonding, (b) after bonding assuming rigid substrate.

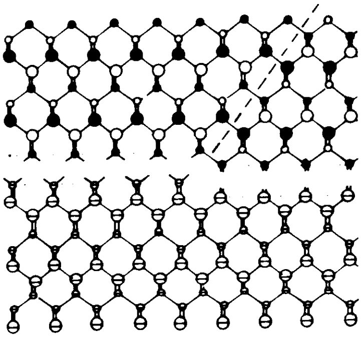

Fig. 6. (110) projection of GaAs:Ge films having complementary (001) surfaces. The dashed line indicates an inversion boundary in GaAs.

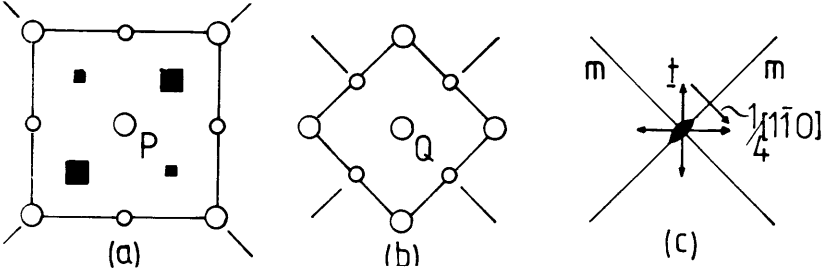

Fig. 7. (001) projection of (a) GaAs and (b) Al unit cells, showing common symmetry operations. The rigid displacement, $\underline{t}$, of the Al, and the equivalent displacements (i.e. those related to $\underline{t}$ by the common operations) are shown in (c); the Burgers vectors of interfacial dislocations, equal to ¼<110>, correspond to the vectors joing equivalent displacements.

if S(e) and S(s) are operations of the same type but which are slightly misoriented in the two crystals. This possibility is illustrated in fig. 5, where mirror planes in the two crystals are misoriented by the small angle ϕ. In the simple case illustrated the mirror plane of the substrate leaves the substrate's surface invariant, but the mirror in the epitaxial layer relates inclined facets. The operation required to bring the substrate surface onto the new epitaxial crystal surface in fig. 5(a) is a rotation of 2ϕ about the axis parallel to the intersection of the two mirrors. It is possible that misorientations of the type described above lead to improved matching of crystal periodicities parallel to the interface, particularly in cases where the matching on low index planes is poor. We note that several papers report small misorientations[10,11,12], although the effect described earlier arising from arrays of steps on the initial substrate surface is another possible explanation of such observations. Preliminary observations using transmission electron microscopy of Pd_2Si:Si films [12] indicate that disclinations may be present.

The nature of the strain around a disclination is quite distinct from that around a dislocation, and is indicated schematically in fig. 5(b). The elastic energies of an isolated dislocation and disclination in homogeneous material are given by $\mu b^2 \ln(R/r_o)/4\pi(1-\nu)$ and $\mu w^2 R^2/16\pi(1-\nu)$ respectively [14], where the symbols μ, b, ν, R and r_o have their usual meaning and w is the angular rotation of the disclination. In the case of a dislocation a large proportion of the energy is stored close to the dislocation core, and the energy increases only logarithmically with the size of the crystal, R. On the other hand, little energy is stored close to the core of a disclination, but this increases parabolically with R. It therefore follows that disclinations may be nucleated fairly readily in very thin epitaxial films, but that a critical film thickness will be reached when the stresses near the growth surface will be sufficiently high to nucleate other defects such as crystal dislocations. We also note that disclinations can move along an interface only by the emission or absorption of dislocations, and may therefore act as dislocation sinks or sources. Finally we note that interfacial disclinations can arise as a result of 'hill and valley' type step structures on the substrate surface. These steps might be accommodated by the overlayer as described earlier, each step acquiring dislocation character following deposition. In particular, the components of the Burgers vectors perpendicular to the surface arising from a 'hill' or 'valley' configuration of steps would correspond to an array of dislocation dipoles. Such an array of dipoles is equivalent to a disclination, and long range stresses would arise. Thus, the configuration of surface features on the initial substrate has a very important bearing on the quality of an epitaxial layer deposited subsequently.

DOMAIN STRUCTURES IN EPITAXIAL LAYERS

The character of interfacial defects delineating the intersection with the interface of domain boundaries in one of the crystals can be treated by substituting the appropriate exchange operations, $[\chi/\underline{\alpha}]$, into expression (1). One application of this approach which has been presented recently [4,15] concerns the occurrence of inversion domains in GaAs films grown on Ge substrates. It will be recalled that the set of exchange operations for the sphalerite structure is twenty four operations having non zero supplementary displacements $\underline{\alpha}(e)$. Moreover, these operations leave the substrate invariant because this has the diamond structure and hence exhibits these symmetries when perfect. It follows that the product $S(e)\ S(s)^{-1} = [\chi(e)/\underline{\alpha}(e)]\ [D(s)/\underline{\alpha}(s)]^{-1}$ will be equal to the identity, [E/0], when the epitaxial exchange operation and the substrate operation have the same form. In other words, when the initial substrate and overlayer surfaces are brought together, the new surfaces will be simultaneously complementary and form an interface with the same energy, as is shown schematically in fig. 6. Thus, the line-discontinuity delineating the intersection of the epitaxial domain