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LETTER TO THE EDITOR

Asymmetric coherent tilt boundaries formed by molecular beam epitaxy

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Abstract. We describe a novel system in which low-angle, asymmetric tilt boundaries organise spontaneously under conditions of molecular beam epitaxial growth. In the cases studied, the $(10\bar{1}2)$ surfaces of hexagonal rare earths grow coherently but tilted on the (211) surfaces of BCC transition metals. The main driving forces are interfacial coherency and the relief of long-range epitaxial strain.

The processes by which crystals adopt low-energy configurations during epitaxial growth remain poorly understood. A thin film may grow strained, owing to its epitaxial registry on a substrate to which its lattice parameter is mismatched [1]. It can find states of lower free energy when dislocations move to the interface to reduce or eliminate the strain [2, 3]. Much of the present quantitative information about the phenomenon and mechanisms of strain relief in epitaxially grown films has been derived from studies of the Si–Ge system [3–6]. The results remain a subject of debate, particularly with regard to the early stages of strain relief [7, 8]. Dislocation motion is sluggish in valence crystals; metals, by way of contrast, exhibit greater dislocation mobility and the strain in epitaxially grown metal films is known [9] to be relieved much more readily. Here we report the discovery of a new system in which dislocations order at polymorphic metal interfaces during the early stages of overlayer growth. In effect, the interface organises itself into a low-angle asymmetric tilt boundary that is coherent and optimally designed to relieve the long-range strain of the epitaxial film. Accordingly, the tilt angle is tunable by selection of lattice constants, and may be predicted quite accurately from geometrical considerations alone. In this way, tilts may easily be tailored in the range 0–7°. The possible role of tilt boundaries in the relief of epitaxial strain has been the subject of a recent paper [10]. The present work establishes that new, simpler, and useful interfacial behaviours are accessible in the growth of strain-relieved materials. Incomplete relaxation has been widely studied, for example in α-Si_3N_4 with Si [10], GaAs on Si [11] and CdTe on GaAs [12]. Crystals commonly rotate in martensitic processes also [13].

Figure 1 illustrates the general process of strain relief that takes place in the films discussed here. The detailed mechanism is more subtle and its description is deferred until the results have been presented. On the left hand side of figure 1 a thin film is shown strained by an applied stress. In the case described here, the actual strain is caused by the size misfit of a rare earth epilayer on a BCC metal substrate. Dislocation motion down active glide planes causes a rotation of the crystal, as shown on the right hand side of

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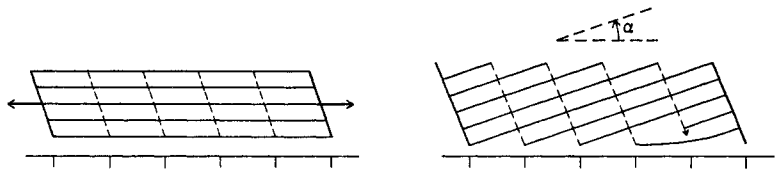

Figure 1. On the left hand side is shown a thin film strained by a tensional (coherency) stress into exactly commensurate registry with a substrate. Potential glide planes are indicated by broken lines. The strain is relieved on the right hand side by dislocation motion down the glide planes, with a consequent tilt of the crystal. One dislocation is shown still moving on the extreme right.

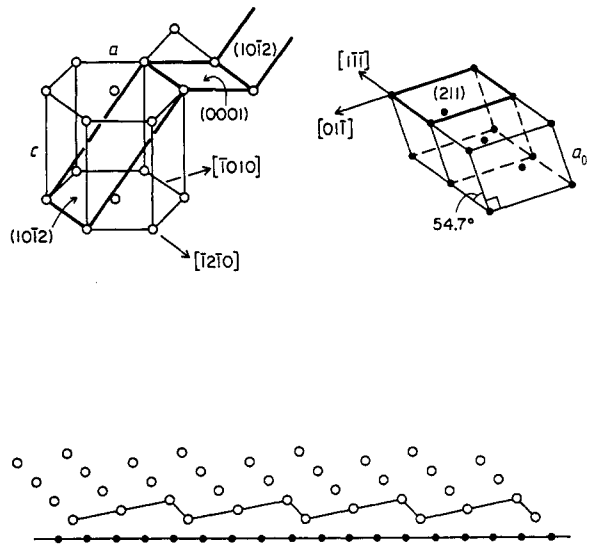

Figure 2. The geometry of the HCP and BCC lattices are shown above, including the lattice spacings a and c for HCP and a_0 for BCC. Heavy lines indicate the BCC (211) plane and the HCP (10$\bar{1}$2) plane, the latter linked by a basal plane segment to a neighbouring (10$\bar{1}$2) plane. Below is shown a low-angle asymmetric tilt boundary (unrelaxed) defined by registry of (10$\bar{1}$2) on (211) with $m = 2$, $n = 4$ (see text). Only one atom per cell of the HCP lattice is shown in the sketches.

figure 1. A correct choice of rotation angle α can relieve the long-range strain completely, and simultaneously bring the two surfaces into commensurate registry as indicated. This asymmetric tilt boundary eliminates the strain energy, and can also reduce the interfacial energy, owing to the surface registry.

In the experiments reported here the substrates were freshly grown (211) surfaces of the BCC transition metals V, Nb and Ta, together with Cr, Mo and Cr–Mo alloys. The structure of this surface is sketched in figure 2. Epitaxial films of the rate earths Y, Gd, Dy, Ho and Lu were subsequently grown on the BCC surfaces. These are all hexagonal close-packed metals. We observe that their (10$\bar{1}$2) planes grow pseudomorphically on the BCC (211) surfaces at the lowest coverage, but tilt away to form an asymmetric tilt boundary as the coverage increases. In this process the [1$\bar{2}$10] tilt axis remains parallel

to the [$\bar{1}$11] azimuth of the (211) BCC surface. The relevant structure of the rare earth lattice is sketched in figure 2, and the relationship between the two surfaces is also clarified there. In hexagonal rare earth metals the (0001) basal plane normally [14] facilitates dislocation glide along [11$\bar{2}$0] and equivalent directions, and these appear to be the active glide systems for strain relief in the present results. Suppose then that one added (0001) plane is required for each m units of surface, with height mc and width $2ma\sqrt{3}/2$ (see figure 2). The total width of a repeat length is thus $(2m + 1)a\sqrt{3}/2$. The HCP surface periodicity must fit coherently with n units of the BCC surface, length $na_0\sqrt{2}$, so that

$$2n^2a_0^2 = m^2c^2 + 3(2m + 1)^2a^2/4. \tag{1}$$

In terms of this same geometry, the tilt angle α may be obtained as

$$\text{cosec } \alpha_n = 2\sqrt{2}n(1 + \lambda^2/3)^{1/2}a_0/c \tag{2}$$

in which $\lambda = c/a$ specifies the HCP lattice geometry.

In the experiments reported here we have investigated the structures that occur in practice by studies of samples grown by molecular beam epitaxy (MBE). For this purpose a Perkin–Elmer system equipped with electron beam hearths was employed. From past work [15] it is known that (211) Nb and Ta grow well on (1$\bar{1}$00) sapphire; this was extended to V, Cr, Mo and Cr–Mo alloys in the present research, but strong facetting inhibited further use of V. For the other metals, very good, flat (211) surfaces were indicated by reflection high-energy electron diffraction (RHEED). For Nb and Ta there is a marked tendency to one-dimensional order along [01$\bar{1}$], with irregular row spacing along the [$\bar{1}$11] direction of easy shear and twinning displacements, although Cr and Mo can differ, with irregular spacing along [01$\bar{1}$]. On these surfaces the rare earths generally grow as very good pseudomorphic monolayers that exhibit progressively stronger facetting with increasing coverage. RHEED evidence of the structure is described below in the discussion of growth mechanisms. By x-ray measurements we have verified that both the rare earth metal and the BCC sublayer form excellent crystals with coherence lengths generally exceeding 700 Å in all directions. This generally encompasses many terrace lengths each $a/\alpha \simeq$ 20–500 Å long, so the interface can be defined with 0.1° precision. As an example, a Brag scan and rocking curves for Y grown on Ta at 600 °C are shown in figure 3. The Bragg peak is $\simeq$0.05° full width at half maximum and the two rocking curves are $\simeq$0.2° wide, using Mo Kα radiation. There is very little added width perpendicular to the tilt axis, which must indicate that the tilt angle is sharply defined.

By means of x-ray scans we have been able to determine the normals to the BCC (211) planes and the HCP (10$\bar{1}$2) planes. The experiments employed a four-circle diffractometer system with a rotating anode source, for convenience in structure analysis. In this way we have measured the tilt angle α for a variety of interfaces, with a typical uncertainty $\pm$0.1°. For the case of Y on Ta shown in figure 3, for example, the tilt is 4.3° directed entirely along the Ta [01$\bar{1}$] azimuth. Using different BCC metals and alloys to vary a_0, and the somewhat smaller variations among different rare earths, we have been able to tune the tilt angle α between 0 and 7°.

For all cases presented here, two BCC units somewhat exceed one rare earth unit. Therefore $n = 2m$, with the remaining length difference accommodated by the tilt

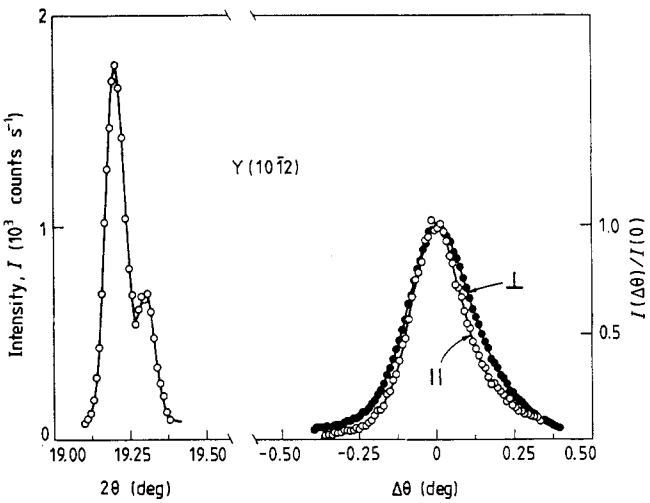

Figure 3. X-ray diffraction peak of Y on Ta (211) showing a Bragg scan and two rocking curves respectively parallel (||) and perpendicular (⊥) to the [1$\bar{2}$10] tilt axis, for the Y (10$\bar{1}$2) peak. The Bragg scan shows the Mo $K\alpha_1$–$K\alpha_2$ splitting.

together with the added unit of basal plane. With this value of m, equation (1) may be solved for n to find from equation (2)

$$\sin\alpha = cy/\{2\sqrt{2}a_0(1+\lambda^2/3)^{1/2}[1+(1+y)^{1/2}]\} \tag{3}$$

in which

$$y = (8a_0^2/3a^2)[1-(3a^2/8a_0^2)(1+\lambda^2/3)]. \tag{4}$$

The factor in square brackets in equation (4) measures the fractional misfit from precise $n = 2m$ registry.

Figure 4 shows the sine of the observed tilt angle, for a variety of samples, as a function of the value of sin α_{th} predicted from (3) by using tabulated lattice spacings for the growth temperature. For this purpose n is treated as a continuous variable, rather than an integer, in the belief that a non-integer average may result from a succession of slightly different integral tilts. The observed tilt angles conform very accurately to the predictions. This shows that the long-range strain is eliminated by a rotation of the rare earth lattice through a mean tilt angle that brings the two lattices into precisely commensurate registry at the interface. In agreement with this wholly geometrical interpretation we note that chemical distinctions between the V and Cr columns of transition metals appear to have no substantial influence whatever on the interfacial structure.

We believe that the films studied here have special properties, unlike most alternative epitaxial systems. Most metallic films relax coherency strains when 100–500 Å thick. By x-ray measurements we confirm that the strain both parallel and perpendicular to the growth direction in 2000 Å films is relieved, typically to 2 parts in 10^3, so the lattice spacings agree with bulk values to this accuracy. The unique feature of the present system is that the relief occurs in an organised way at thicknesses $\geqslant 20$ monolayers, by a specific symmetry-breaking rotation of the epilayer that simultaneously relieves the strain and makes the interface commensurate. The findings for these materials differ

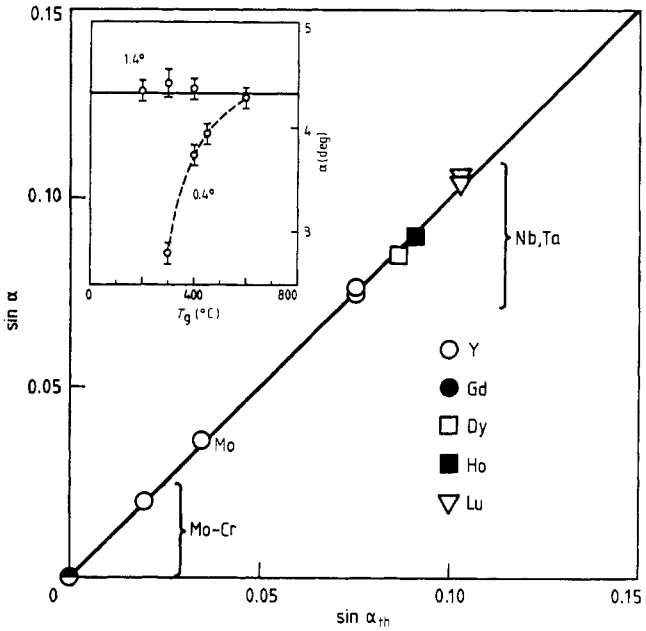

Figure 4. The observed and calculated tilt angles are compared for a variety of rare earth metals and BCC sublayers. There is very good agreement between the data (points) and the theory (line). Inset is shown the dependence of observed tilt angle on rare earth growth temperature T_g and sapphire substrate miscut (in degrees, given next to the points) for Y on Ta (the horizontal line indicates the calculated tilt angle).

markedly from interesting results for Ag(100) and Fe(100) grown on GaAs(100) by Farrow *et al* [16]. There the Fe is *not* relaxed, which is attributed to a low growth temperature, and the tilts differ from simple reductions by a large factor.

While the cause and structure of these tilt boundaries thus appear reasonably well understood, the detailed mechanisms by which they assemble themselves under conditions of MBE growth remain still to be discussed. RHEED evidence, e.g., for the case of Y on Ta at 400 °C shows that the surface with about 40 Å of Y exhibits strongly tilted $(10\bar{1}2)$ terraces, indicated by angled streaks. It seems probable that such tilts reflect the gradual creation of interace structure by dislocation motion, as suggested by figure 1. A point of special interest is that the BCC (211) surface plane has mirror symmetry about $(01\bar{1})$. The observed tilt thus represents a symmetry breaking in which one of two equivalent rare earth stacking sequences (and hence glide planes also) prevails. We have verified that the symmetry is broken by the sapphire substrates, which are typically miscut by $\simeq 1°$ from $(1\bar{1}00)$. The component of the miscut along $[11\bar{2}0]$ establishes a prevalent orientation of the surface ledges, and hence a particular direction of ledge motion under MBE conditions of ledge growth [17, 18]. We anticipate that the ledge structure and growth direction is directly replicated in the BCC sublayer and the rare earth film successively. When approaching a region of buried strain, a rare earth ledge growing across microdomains of the two twins then typically meets one particular glide plane first. The consequent bias apparently causes the cooperative selection of one particular tilt (less than 0.1% of the opposite tilt is observed by x-rays). Our x-ray measurements show that the rare earth planes are always tilted away from the BCC planes

in the *opposite* sense from the tilt of the BCC sapphire interface from the BCC planes (i.e. the sapphire miscut), just as this description would suggest.

In connection with the kinetics of interface formation it is worth noting that the tilt angle exhibits a weak additional dependence on growth temperature T_g, and sapphire cut. The results inset in figure 4 show, for Y on Ta, how the tilt angle departs from the ideal value for $T_g \leqslant 550$ °C when the sapphire is miscut along $[11\bar{2}0]$ by $\simeq 0.4°$, whereas it remains near its ideal value down to 200 °C when the miscut is 1.4°. In both cases, the fraction of the 'wrong' tilt increases with decreasing growth temperature, as do the x-ray widths. These effects may well refect changes of dislocation mobility as well as the kinetics of atomic assembly. We expect that a more detailed understanding of the structures will be forthcoming once electron micrographs of the interfaces are available. Efforts to achieve this goal are currently progressing, but are made difficult by the hardness of α-Al_2O_3 and the reactivity of the rare earth metals.

To conclude one may reasonably inquire whether interfacial phenomena with the simplicity and precision of these tilt boundaries are truly as rare as the literature would suggest [19]. One comparable case is the tunable angular *twist* misorientation exhibited [20, 21] by incommensurate rare gas monolayers weakly coupled to hexagonal surfaces. Epitaxial growth is again involved, but the phenomenon concerns surface registry alone. Our tilt boundaries are quite different in that they self-assemble at higher coverage as a consequence of the long-range strain. In this connection, research that employs epitaxial films to study interfacial effects is favoured over bulk studies by the accessibility of large coherent strains in specimens with at least one small dimension with which to facilitate rapid atomic transport or plastic relief. Again, while group IV and III–V materials are not very ductile, metals are favoured by easy dislocation motion and by low growth temperatures. It may well transpire that comparable phenomena occur much more widely than is currently recognised in systems that possess similar advantages. Developments of this type could find a variety of useful technical applications in the synthesis of new structures, including tilted superlattices and atomic chains, or for the growth of crystals at unusually low temperatures. By spatial variations of substrate composition it may prove possible to grow Fresnel mirrors for application in neutron and x-ray optics.

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