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Slip requirements for coherent tilt of hcp epitaxial crystals

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By preparing epitaxial layers of various hcp metals we explore the plastic behavior required to grow epitaxial crystals with atomic planes tilted from the substrate planes in the predictable and tunable way described earlier by Du and Flynn. Explicit requirements for coherent tilt are formulated.

Du and Flynn (DF) report that hcp rare-earth crystals can be grown epitaxially on bcc substrates with their atomic planes tilted with respect to those of the bcc substrate.[1] The process is specific to the $(10\bar{1}2)$ planes of rare earths, which grow tilted on the "magic" (211) planes of bcc transition metals. This tilt is coherent over the entire epitaxial film. Its axis and angle are precisely reproducible and can be predicted and tuned with 0.1° accuracy by means of the lattice spacings of the two metals. The predicted tilt angle is

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

in which

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

Here, a_0 is the bcc lattice spacing and $\lambda = c/a$ specifies the hcp geometry. In practice, the unstrained rare-earth lattice spacing is a little too small to fit the substrate. What happens is that the final epilayer is fully strain relieved, but has its planes tilted at the angle needed to recover a coherent interface, and this requirement fixes the tilt in Eq. (1). Tilt angles in the range 1–7° were observed, and could be predicted from these ideas. The facts point to a mechanism in which the tilt is driven by the strain energy of the initially pseudomorphic film. In more recent work Du and Flynn have investigated the evolution of the epitaxial strain with film thickness.[2] They find that the rare-earth suffers an initial one-dimensional (1D) positive pseudomorphic strain oriented along the $[01\bar{1}]$ azimuth of the bcc (211) substrate surface, which itself grows with 1D order. The strain thus defines the tilt axis, and its relief directs the mechanism by which tilt takes place. The necessary symmetry breaking, by which only one of the two alternative rotation senses is selected coherently over the entire substrate, is dictated by the substrate miscut through step-edge flow mechanisms mentioned below. These pseudomorphic and symmetry-breaking processes are apparently two key factors in the observed remarkable tilt behavior.

A third essential ingredient is the process of strain relief itself, which remains less well understood. The investigations reported below were undertaken in an effort to learn more about the mechanisms by which tilt takes place. From a broader perspective it is worth noting that epitaxial tilts are observed in nonmetals also,[3] but not yet in the reproducible or predictable form of interest here. The fact that essentially complete strain relief occurs in the present case may presumably be explained by the relatively easy motion of dislocations in metals as contrasted, for example, to the case for semiconductors. Electron microscopy offers promising opportunities to examine the tilt process but, in practice, the difficulties of handling and thinning reactive rare earths have slowed our efforts to explore the tilt process in this way. Here we offer an alternative approach. The direction of possible $[11\bar{2}0]$ (0001) dislocation slip in hcp rare earths[4] is very well oriented for the relief of the 1D pseudomorphic strain of the $(10\bar{1}2)$ plane described above, because the (0001) slip plane falls at about 38° to the strain axis and the $[11\bar{2}0]$ slip itself occurs at about 50° to the axis; these geometrical relationships are shown in Fig. 1(a). Information about the plas-

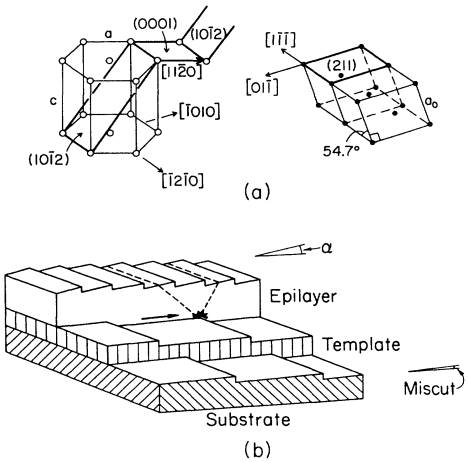

FIG. 1. (a) The hcp (left-hand side) and bcc (right-hand side) lattice geometries relevant to the growth of tilted $(10\bar{1}2)$ planes. (b) Sketch showing a miscut substrate (bottom) with successive bcc template and tilted epilayer. The miscut causes step flow in a unique direction, so that the growing material reaches one particular orientation of slip plane (dashed lines) first.

tic behavior of the rare earths is, however, quite limited both in scope and in its uncertain sensitivity to temperature and to impurities present in the tested materials. Our chosen goal was therefore to synthesize films using other hcp metals with various preferred slip characteristics that are well established, to see how their plastic properties influence the resulting expitaxial structure. To this end we selected three systems: magnesium, which favors slips primarily in the basal plane,[5] and titanium and zirconium which do not, preferring instead slips across the prism plane,[6] which is orthogonal to the epitaxial strain. The results in brief are that while Mg exhibits coherent tilt just like the rare earths, neither Ti nor Zr conform to this ideal behavior. In this way the work reported in what follows points to the $[11\bar{2}0]$ (0001) slip system as a central ingredient of the controlled tilt process described by DF.

Our experimental studies were undertaken using substrates of epitaxial grade sapphire with $(1\bar{1}00)$ surfaces miscut by about 1.5° along $[11\bar{2}0]$. There is convincing evidence[1] that the initial symmetry breaking which determines the direction, positive or negative, of the coherent tilt about the bcc $[\bar{1}11]$ axis, is fixed by the substrate miscut together with the conditions of ledge growth under which the epitaxial layers are created. These cause ledges to move over the surface in only one of the two senses perpendicular to the $[\bar{1}11]$ tilt axis. Tilt must then take place by the glide of dislocations through the film, thereby rotating the lattice planes and relieving the epitaxial strain. If the dislocation process responds to existing strain inhomogeneities, the directed step-flow growth biases the resulting selection between otherwise equivalent glide planes of the pseudomorphic film. A schematic representation of the resulting structure is provided in Fig. 1. The present choice of a 1.5° miscut along $[11\bar{2}0]$, retaining less than about 0.2° miscut about the orthogonal direction, is believed close to optimal for these purposes. The substrates were annealed for at least 30 min at 1150 °C to minimize surface disorder prior to metal growth.

Details of the chamber in which annealing and subsequent growth took place are provided elsewhere.[7] Two *e*-beam sources capable of evaporating any desired metals were employed in the present work. The substrate could be maintained at any required temperature in the relevant range. Even during growth of refractory materials the pressure remained in the range below 10^{-9} torr. Therefore, to the best of our knowledge, the phenomena reported here are intrinsic, with impurity contamination playing no part in determining the observed epitaxial behavior.

Mg was grown on Mo because a large, convenient tilt angle of 7.32° between the Mg$(10\bar{1}2)$ and Mo(211) planes is predicted by Eq. (1). First a Mo film 50–100 nm thick was grown at 0.05–0.2 nm/sec at a growth temperature of about 900 °C. Reflection high-energy-electron diffraction (RHEED) observations indicated that the bcc surfaces adopted configurations with regular steps. This behavior is illustrated by the splitting of RHEED streaks[8] evident, for example, in Fig. 2(a). The circular arrangement of short streaks indicates the surface is relatively smooth over the electron coherence length ~100 Å. One-dimensional order was much less visible on Mo(211) than in earlier studies of Ta and Nb.[1,2] Mg exhibits little

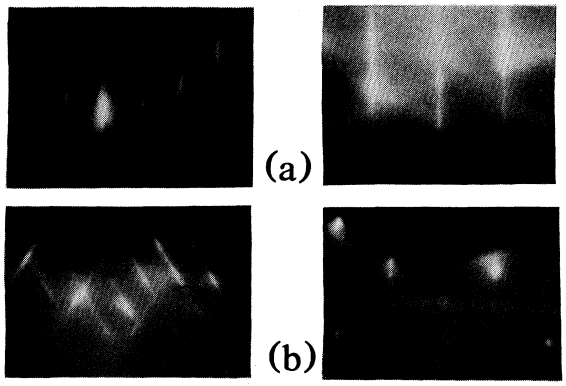

FIG. 2. RHEED pattern showing (a) Mo(211) along the $[1\bar{1}1]$ tilt axis (left-hand side) with visible splitting from regular steps, and along [011] (right-hand side). This is a smoothly tilted surface that does not exhibit clear 1D order. In (b) the pattern for 20 monolayers of Mg on Mo is shown with angled streaks along the $[1\bar{1}1]$ azimuth, demonstrating the facetted Mg surface, and some 3D character in the perpendicular direction (right-hand side) from the beam penetrating the facets.

solubility in transition metals, including Mo.[9] Therefore a sharp Mo-Mg interface is to be anticipated. In practice, Mg was grown from an effusion cell on the fresh, stepped Mo surface at growth temperatures ranging from 50–180 °C. For growth temperatures over 200 °C the rate of thermal desorption of Mg became significant compared to typical growth rates below 0.1 nm/sec. The initial monolayers of Mg growth were seen to exhibit 1D pseudomorphism entirely analogous to that of the rare earths. After several monolayers of deposition the Mg was observed to tilt. The outer surface then formed (0001) and $(10\bar{1}1)$ facets similar to earlier observations for Y grown on Ta at the relatively low temperature of 100 °C. The RHEED pattern from this surface is shown in Fig. 2(b). We believe that the sharpness of the RHEED streaks may indicate that the Mg is clustering on the surface to a significant extent.

X-ray scans made using a Huber four circle diffractometer establish that the Mg forms an excellent single crystal. For a film 0.3 μm thick using Mo radiation, the Bragg and rocking scans of widths 0.06° and 0.15°, respectively, point to a structural coherence length about 0.1 μm in all directions. The tilt of the Mg $(10\bar{1}2)$ from the Mo(211) plane, averaged over four independent samples, was observed as $7.35 \pm 0.1°$. This is in good agreement with the value of 7.32° predicted using Eq. (1). Although rather dissimilar from rare earths in many physical properties, Mg thus displays epitaxial behavior on bcc (211) planes very similar to that of the rare-earth metals.

Zirconium and titanium differ from the rare earths and magnesium in that they exhibit primary $(10\bar{1}0)$ $[11\bar{2}0]$ prismatic slip characteristics with basal plane slip much less favored. Characteristics of this type correlate strongly with the hcp c/a ratio,[10] and the materials investigated here conform to these general patterns of behavior. The differences are of special interest in the present context as

shear strains across the $(10\bar{1}0)$ planes are all orthogonal to the pseudomorphic shear of a $(10\bar{1}2)$ epilayer. Therefore prismatic slip is unable to relieve the pseudomorphic strain, and cannot contribute to the tilt mechanisms of concern here.

In our experiments Zr was grown on Mo, Ta, and on Cr. The Mo and Ta were freshly prepared as above. It was necessary to grow Cr on a Mo(211) buffer layer because its misfit from sapphire is too large to accommodate direct growth of good material. Upon appropriate surfaces Zr grows well at about 450 °C. We found that Zr on Mo(211) grew with cloudy RHEED patterns as a textured polycrystalline film containing $(10\bar{1}0)$, $(10\bar{1}2)$, and $(10\bar{1}3)$ orientations among others, rather than as a tilted single crystal. Much the same result was found for Zr on Ta even when grown at temperatures up to 600 °C. Elongated one dimensional streaks together with a tendency to three dimensional spots persisted in the RHEED patterns. Evidently these surfaces became mosaics of different $(10\bar{1}l)$ orientations without reaching the relaxed coherent state. On Cr(211), on the other hand, Zr$(10\bar{1}2)$ was found as hoped but the prediction from Eq. (1) of tilt at 3.42° did not agree with the observed essentially zero tilt of $0 \pm 0.2°$. The Zr outer surface facetted mainly into $(10\bar{1}1)$ and (0001) components, much as in the case of Mg, but the bulk surface retained the untilted $(10\bar{1}2)$ orientation. In all the examples described here the film growth continued far beyond the point at which any possible interdiffusion could influence the epitaxial strain. At least two independent samples of each type were grown and examined to confirm the results presented here.

Over the past several years we have made extensive efforts to grow Ti on bcc transition metal surfaces, as summarized elsewhere.[11] The behavior on Ta(211) and Mo(211) provide but three of the six distinct orientations of high quality Ti single crystal epilayers grown in our recent studies. On Mo(211) at 400 °C, Ti grows in the untilted $(10\bar{1}3)$ orientation rather than the $(10\bar{1}2)$ orientation tilted by 10.8° predicted by Eq. (1). On Ta(211) it grows on the $(10\bar{1}0)$ plane untilted at temperatures in the range 250–350 °C. At 400 °C and above it does grow instead of the $(10\bar{1}2)$ orientation of concern here. However, the observed tilt angle of 10.7° differs significantly from the value of 12.4° predicted by Eq. (1). The evidence for Ti on Ta(211) is interpreted[11] as indicating that Ti$(10\bar{1}0)$ nucleates on the Ta terraces at low temperature. At high temperatures, and consequently high atomic mobilities, the added species diffuse rapidly enough to reach and nucleate at the step edges at which the terraces terminate. It turns out that the observed 10.7° tilt is close to the value of 10.3° predicted from the geometrical matching condition between the 3D structures at the step edges.

In the light of the investigations reported here, the present understanding of the mechanism for the coherent tilt process reported by Du and Flynn may be summarized as follows. To date the $(10\bar{1}2)$ growth of eight hcp metals has been studied, now including Mg, Zr, and Ti, in addition to the rare-earth metals, Y, Gd, Dy, Er, and Ho studied by DF. Many of these have been grown on several different transition metal (211) surfaces. The five rare earths and Mg, the latter known with certainty to exhibit easy basal plane slip, in all cases yield tilted $(10\bar{1}2)$ oriented single crystal epilayers. In each case the tilt angle was determined to be within an uncertainty of 0.1° of that predicted by DF for the relevant lattice spacings. The metals Zr and Ti, on the other hand, are well known to exhibit predominantly prismatic slip. When deposited on bcc (211) surfaces these metals grow in several forms, including polycrystalline and various alternative single crystal orientations, but never, as yet, in the tilted $(10\bar{1}2)$ orientation with the tilt appropriate for a fully relaxed crystal with a coherent interface.

We conclude that the coherent process whereby hcp metals grow with a reproducible and predictable tilt on the "magic" (211) planes of transition metals depends on three principal requirements. First is the positive 1D pseudomorphic strain that stores the misfit energy and channels its release towards appropriately directed slip processes. The second requirement, established in the present work, is for easy slip down an appropriately oriented plane, in this case the basal plane, in order that dislocations can relieve the pseudomorphic strain and in doing so rotate the epilayer into the desired, fully relaxed, coherent configuration. Given these two materials-specific requirements, a third, geometrical constraint must be imposed on the system. For pseudomorphic systems with mirror or inversion symmetry it is necessary to miscut the substrate along the direction of pseudomorphic strain in order to select a single sense of cooperative rotation of epilayer planes over the entire substrate surface.

In elucidating these requirements and their interrelationships we seek a broader understanding of growth mechanisms and improved control of the epitaxial structure. It is clearly an interesting and useful challenge, for example, to apply the present understanding in efforts to prepare other crystal faces or different crystal structures under conditions of controlled coherent tilt.

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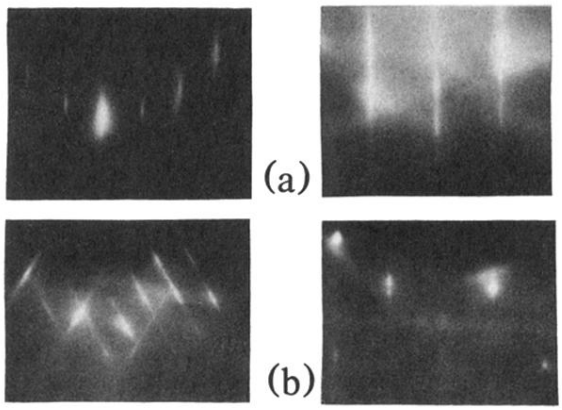

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