adsorbate–adsorbate interactions is not merely to order atoms into particular arrangements on an adsorption checkerboard determined by the substrate (see Chapter 11). Now these interactions determine a 'natural' lattice constant for the overlayer material. In the simplest case, we seek the lowest energy 'arrangement' of such a lattice forced into contact with a substrate which exhibits a different lattice constant. Interesting complications arise if one permits one (or both) lattices of this bicrystal to be elastically non-rigid. As we shall see, these considerations have important implications for the growth of artificial materials.

**Orientation and strain**

Early experimental studies of crystal growth showed quite clearly that there exist preferred orientational relationships between dissimilar crystal lattices when they are forced into intimate contact (see e.g., Seifert (1953)). It turns out that one can rationalize the observations on the basis of purely geometrical 'row-matching' considerations. Consider the case of a bicrystal formed by the placement of a close-packed FCC(111) monolayer (nearest neighbor distance \( a \)) atop the close-packed (110) surface of a BCC substrate (nearest neighbor distance \( b \)). For the orientation depicted in Fig. 16.1(a), it is easy to see that consecutive atomic rows parallel to the

Fig. 16.1. Overlay of an FCC(111) monolayer (filled circles) onto a BCC(110) substrate surface (open circles): (a) FCC [011] parallel to BCC [001]; (b) 5.26° rotation relative to (a). The lattice constants of the two crystals are chosen to produce row-matching in the rotated case (Dahmen, 1982).
The KS and NW orientational relationships are observed for many metal–metal adsorbate–substrate combinations (Bauer, 1982). Of course, this does not mean that the natural lattice constants are in precisely the ratios predicted by Fig. 16.2. Generally there is some non-zero ‘misfit’ \( f = (a - b)/a \). Epitaxy occurs because the overlayer material distorts somewhat to achieve row-matching. The reader will recall that this terminology arose earlier in connection with our discussion of the commensurate–incommensurate transition in physisorbed overlayers (Chapter 11). In that context, we saw that for small values of misfit, the overlayer strains to match itself to the rigid lattice constant of the substrate. Domain wall defects appear for larger values of \( f \) (Fig. 11.10). The same occurs here except that a new feature – KS rotational epitaxy – enters by virtue of the two-dimensionality of the problem. As a matter of fact, rotational epitaxy occurs for the case of incommensurate physisorbed overlayers as well. It is instructive to examine the connection between the two.

The essential ingredient is the interaction energy between a rigid substrate (reciprocal lattice vectors \( \mathbf{G} \)) and a non-rigid overlayer lattice (reciprocal lattice vectors \( \mathbf{g} \)). By ‘non-rigid’ we mean that the atoms of the overlayer are permitted to strain away from their equilibrium positions. For small excursions, an approximate energy expression is:

\[
\frac{E}{N} = \sum_{G \in \mathbf{G}} V_G \delta_{G\mathbf{G}z} - \frac{1}{2} \sum_{G \in \mathbf{G}} V_G u(q) \cdot \mathbf{G} \delta_{G\mathbf{G}z} + \frac{1}{2} \sum_{G \in \mathbf{G}} h_{\text{dis}}(q) \delta_{G\mathbf{G}z} \tag{16.1}
\]

The first term we have seen before (cf. (11.7) and (11.8)). It is present whether strain is present or not and, in effect, is all that enters the Lennard-Jones calculations discussed above. Now let \( u(q) \) denote the Fourier components of some static displacement pattern which the overlayer may wish to adopt. The second term (made plausible from dimensional analysis alone) describes the energy gain associated with this distortion while the third term counts the energy cost (McTague & Novaco, 1979). The latter is expressed in terms of the phonon frequencies \( \omega(q) \) of the overlayer.

By definition, the first terms vanish for an incommensurate overlayer. The lowest energy configuration then represents a compromise between the remaining two terms. This picks out one particular \( q \)-vector which, from the delta function restriction, picks out a preferred angle \( \theta \) between the vectors \( \mathbf{G} \) and \( \mathbf{g} \). If the two real-space lattices have the same symmetry (as in our examples below) this shows up as a simple rotation of the overlayer with respect to the substrate by exactly the angle \( \theta \). LEED experiments directly test such predictions (Fig. 16.3) since one can vary the natural lattice constant of the overlayer (and hence the misfit) simply
by changing the coverage. Note that the theory appears to account for data from not only a bona fide incommensurate system – physisorbed Ar/graphite – but also for a strong chemisorption system – Na/Ru(100).

For commensurate systems, it is necessary to consider explicitly the first term in (16.1). At 1/3 coverage, this 'lock-in' energy stabilizes the \((\sqrt{3} \times \sqrt{3} - 30^\circ)\) structure of Na/Ru(100). But, as the coverage increases, more sodium atoms must occupy chemisorption sites. Where do the atoms go? It is easy to convince oneself that (at any coverage) it is always possible to find a commensurate overlayer structure (with unit cell axes rotated from the substrate axes by some angle) with a \(g\)-vector that matches to some \(G\)-vector of the substrate. Of course, the requisite overlayer unit cell might be very large. Nonetheless, one can always gain some lock-in energy.

On the other hand, glance back at Fig. 11.15 and recall our discussion of the commensurate–incommensurate transition. The key idea there was that a commensurate solid interspersed with extra atoms ('domain walls') can be regarded equally well as an incommensurate solid. Consequently, the foregoing analysis will remain correct for high-order commensurate structures if the strain terms in (16.1) successfully compete with the lock-in term.

Return now to the FCC(111)/BCC(110) epitaxy problem where lock-in dominates the problem and NW and KS orientational relationships are the rule. This does not imply that strain effects are insignificant. In fact, a vast richness opens up with just the slightest allowance for atomic relaxation. Fig. 16.4 presents a structural phase diagram for this problem where only a small number of possible strain patterns have been considered. The parameter \(\lambda\) is a measure of the ratio of intralayer coupling strength to interlayer coupling strength. Hence, near \(\lambda = 0\), the overlayer is strained into commensurability (or 'coherence') with the substrate regardless of the lattice mismatch. Unstrained KS or NW behavior occurs nowhere. In general, the film achieves row-matching only in an average sense. Coherence is lost through a complicated interplay of domain walls along one direction and non-uniform strains in the other. In analogy with the bulk, the former are called 'misfit dislocations' in this context because they appear as added rows of atoms arranged in periodic arrays (Fig. 16.5).

The results of Fig. 16.4 notwithstanding, it is imperative to minimize

Fig. 16.3. Rotational epitaxy of Ar/graphite (triangles) and Na/Ru(100) (circles) as a function of overlayer lattice misfit. Solid curve is the prediction of the last two terms of (16.1) (Shaw, Fain & Chinn, 1978; Doering & Semancik, 1984).

![Diagram showing structural phase diagram of FCC(111)/BCC(110) bicrystal as a function of geometrical \(r\) and energetic \(\lambda\) parameters of the system. Dark shading denotes regions of one-dimensional coherence. Light shading denotes regions where all coherence with the substrate is lost. See text for discussion (Stoop & Van der Merwe, 1982).]
the density of misfit dislocations present at a bicrystal interface if issues of electrical transport are important. Dislocations scatter electrons and hence reduce mobility. For this reason, artificial semiconductor materials generally are constructed from constituents which (a) have the same bulk crystal structure and (b) are as nearly lattice-matched as one can arrange (see, e.g., Bean (1985)). But this may not always be an option. Suppose one desires a heterostructure fabricated from two materials which differ markedly in both crystal structure and lattice constant. Usually, this leads to a mess, i.e., no epitaxy. However, in certain cases, nature has arranged an elegant solution.

Pseudomorphy refers to a situation where the overlayer material adopts a crystal structure and lattice constant which differ from their normal bulk manifestations but which match coherently to the underlying substrate. This is the normal state of affairs in submonolayer chemisorption but is highly non-trivial to arrange when the atoms of the deposit material are within a few Ångströms of one another. For example, elemental tin adopts its familiar body-centered tetragonal ‘white tin’ structure at room temperature. It is a metal with a lattice constant of 5.83 Å. However, the same material crystallizes into the ‘grey tin’ diamond structure ($a = 6.49$ Å) when deposited onto (100) surfaces of InSb and CdTe ($a = 6.48$ Å). There is essentially no misfit at the epitaxial interface and, since grey tin is a semiconductor, one has fabricated a novel heterojunction material (Farrow, 1983). Up to a point that is. The overlayer grows as one adds more material until eventually at some thickness (∼$0.5 \mu m$ in this case) the tin transforms to its bulk stable phase – as it must.

**Crystal growth**

The growth of a perfect semiconducting tin crystal at 300 K as imagined above contains a crucial hidden assumption. It is presumed that growth proceeds in a two-dimensional fashion, one monolayer after the next, up to some desired thickness of overlayer material. As it happens, this actually appears to be the case for Sn/InSb(100) and Sn/CdTe(100). However, it is not the usual situation observed for either the growth of metals on metals (Vook, 1982) or for the growth of metals on semiconductors (Ludeke, 1984). Instead, one often finds that the deposited material ‘balls up’ into three-dimensional clumps which only later coalesce into a thick polycrystalline film. In fact, extensive experimental results point to the existence of three distinct growth modes, each named after investigators associated with their initial description: Frank–Van der Merwe (FV) growth, Stranski–Krastanov (SK) growth and Volmer–Weber (VW) growth.

Fig. 16.6 is a schematic representation of the common modes of crystal
Crystal growth

growth one observes under typical deposition conditions (MBE, MOCVD, etc.). FV growth follows the layer-by-layer scenario outlined above. VW growth is just the opposite. Three-dimensional crystallites nucleate immediately upon contact and the overlayer may not completely cover the exposed substrate surface until a great many atoms have been deposited. SK growth lies in between: a few monolayers adsorb in layer-by-layer fashion before three-dimensional clumps begin to form. The obvious question is: how does one know what sort of growth one is dealing with?

Fig. 16.7. Growth of GaAs(100) by MBE. Intensity of the RHEED specular beam as a function of time (top panel). The slow decay of peak intensity reflects a gradual increase in surface roughness. The lower panel illustrates a model of monolayer growth in the Frank–Van der Merwe scenario (Neave, Joyce, Dobson & Norton, 1983).

Epitaxy

High-quality layer-by-layer growth is essential for the production of electronic materials by molecular beam epitaxy. The in situ UHV technique of RHEED (reflection high energy electron diffraction) appears to be a reasonably reliable monitor of the presence or absence of FV growth. In RHEED, a 5–50 keV electron beam is directed towards the sample at extreme grazing incidence. Electrons scattered through small angles sample only the top 1–2 atomic layers of the crystal under these conditions. The characterization experiment is straightforward: one simply monitors the variation of the specular beam intensity as a function of time. An example is reproduced as the top panel of Fig. 16.7 for the case of GaAs growth with MBE.* Remarkably, the signal exhibits extremely regular oscillations whose period exactly corresponds to the growth rate of a single layer of GaAs (as determined independently). The lower panel of Fig. 16.7 suggests a simple interpretation in terms of FV growth: reflectivity maxima correspond to scattering from atomically smooth surfaces near θ = 0 and

Fig. 16.8. Time dependence of Mo and Cu Auger peak intensities as Cu grows epitaxially on Mo(100). See text for discussion (Soria & Poppa, 1980).

* We need only control the atomic Ga beam in the presence of a continuous supply of arsenic to study this problem since the sticking of As is the rate-limiting step in GaAs growth (Chapter 15).
\( \theta = 1 \) while reflectivity minima correspond to scattering from maximally disordered surfaces near \( \theta = 0.5 \). No persistent oscillations are expected for either SK or VW growth.

Auger spectroscopy is another common technique used to identify epitaxial growth modes. Fig. 16.8 illustrates the time dependence of the strength of two peaks in the Auger spectrum collected from a Mo(100) surface during deposition of copper atoms from a vapor source. Notice that both the increasing Cu signal and the decreasing Mo signal consist of a sequence of line segments with uniformly decreasing slope. We certainly expect linear behavior if a single monolayer of adsorbate uniformly covers the layer beneath it. But, since only those electrons within about one escape depth of the surface actually emerge, the slope of the signal must decline as each new layer is added. In the limit of a thick overlayer, the substrate signal vanishes and the adsorbate signal has zero slope.

Based on escape depth data (Fig. 2.1), the dashed curves in Fig. 16.8 are the predicted Auger amplitudes for Cu/Mo(100) if FV growth is operative. Evidently, the data follow these predictions for at least three layers. The observed behavior is indicative of the Stranski–Krastanov growth mode. It is easy to see, as well, that the Auger technique is sensitive to the difference between SK growth and VW growth. However, sometimes direct inspection is sufficient. The electron micrograph of lead crystallites adsorbed onto a single crystal graphite surface discussed first in Chapter 1 (Fig. 1.7) clearly shows that these solid ‘droplets’ do not ‘wet’ the substrate surface.

For obvious reasons, a good deal of effort has been expended in pursuit of a tractable theory of crystal growth. We encountered some of this work previously in our analysis of the roughening transition (Chapter 1). This example is typical in the sense that, in order to simplify the statistical mechanics, one adopts extremely simple models which hopefully admit analytic solutions. On the other hand, we have seen throughout this book that certain delicate matters of principle can depend quite sensitively on details of the systems under investigation. This observation leads to the prediction that the emphasis in theoretical analysis of epitaxial growth is likely to shift toward molecular dynamics simulations as supercomputer availability increases.

We conclude with an example which illustrates both the power of simple analysis and a clear source of the sensitivity to parameters which bedevils our subject. Let us try to estimate when any one of the three growth modes examined above is likely to occur. To do so, consider the energy difference between the two epitaxial overlayer arrangements depicted in Fig. 16.9. The inputs to this calculation are three macroscopic surface tensions: \( \gamma_0 \), \( \gamma_1 \) and \( \gamma_2 \) – the free energy/unit area at the overlayer–vacuum interface, the overlayer–substrate interface and the substrate–vacuum interface, respectively. We may assume, without loss of generality, that the Volmer–Weber cluster occupies half the available surface area \( A \). It follows immediately that

\[
\Delta E = E_{\text{FV}} - E_{\text{VW}} = (\gamma_0 + \gamma_1)A - \frac{1}{2}(\gamma_0 + \gamma_1 + \gamma_2)A.
\]  

(16.2)

Therefore, we expect complete wetting (FV growth) when \( \Delta \gamma = \gamma_0 + \gamma_1 - \gamma_2 < 0 \), VW growth when \( \Delta \gamma > 0 \) and SK growth when \( \Delta \gamma \approx 0 \).

It is important to bear in mind that this estimate is only qualitatively useful because we have completely neglected any effects which might arise from the anisotropy of the surface tensions (Fig. 1.8). Even then, it is not entirely clear what one should choose for \( \gamma_i \) for any particular epitaxial pair. Existing methods of measurement (see, e.g., Eustathopoulos & Joud, 1980) rely on bulk grain boundary data which are not obviously transferable to the epitaxial situation of interest where additional contributions from misfit dislocations, strain, etc., might be significant. A truly microscopic replacement for (16.2) is yet another challenge for the future of surface physics!

General references

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