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Stacking sequences in close-packed metallic superlattices

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The ground-state stacking sequences of superlattices formed from two dissimilar close-packed metals are studied within the context of a simple tight-binding model. The main result is that the chemical potential for a stacking fault is a Friedel-like, damped, oscillatory function of its distance away from a bimetallic interface. Accordingly, a superlattice compositional boundary can favor unusual stacking-fault configurations and the bulk stacking structure of the constituent metals may not be a good guide to the structure of the superlattice. Application is made to recent diffraction data for ruthenium-iridium superlattices.

In recent years, increasing attention has been directed toward synthetic modulated structures fabricated from combinations of dissimilar metals.[1] By and large, metallic superlattices have been difficult to grow with the structural quality typical of semiconductor heterostructures. Nevertheless, reasonably high quality structures have been prepared when the two metals have the same crystal structure and are well lattice matched, e.g., Nb-Ta.[2] Another promising avenue of attack involves structures grown by alternate deposition of two different close-packed metals with similar lattice parameters. Indeed, Cunningham and Flynn[3] recently have reported x-ray diffraction data from high-quality Ru-Ir superlattices. In their study, the ruthenium (hcp in the bulk) layer thickness was held fixed at about 10 atomic planes while crystals were grown with variable iridium (fcc in the bulk) layer thickness. Unexpectedly, the Ir was observed to transform to hcp when the compositional wavelength became sufficiently small (about 5 Ir atomic planes). In the present Communication we will show that such behavior is, in fact, not surprising and we discuss the general structure that close-packed superlattices are likely to adopt.

Any close-packed structure can be regarded as a particular stacking of hexagonal lattice planes.[4] At each step in the stacking, we require the atoms of a given plane to sit above triangular interstices of the plane below. This rule defines three possible stacking positions, commonly denoted *A*, *B*, and *C*. The fcc structure corresponds to the stacking sequence . . . *ABCABC* . . . while hcp corresponds to . . . *ABAB* . . . stacking. More complicated periodic stacking sequences, known as *polytypes*, also can occur. For example, elemental lithium and samarium crystallize into the so-called 9*R* structure, . . . *ABCBCACAB* . . . .[5] In the following we frequently will use an alternative notation that labels each plane by the letter *h* if its nearest neighbors are identically stacked (e.g., the *B* plane in *ABA*) or the letter *c* if the nearest-neighbor planes differ in stacking (e.g., the *B* plane in *ABC*). In this notation, the 9*R* structure is written . . . *hhc* . . . .

Previous studies[6,7] of the *bulk* properties of close-packed simple metals have shown that the ground-state stacking sequence is a sensitive function of the occupancy of the conduction band (i.e., the valence). In particular, alloys can undergo an fcc→ hcp transition (or the reverse) as a function of composition that proceeds through a sequence of polytypes that "interpolate" between the two end-point structures. The structural stability of these intervening stacking structures arises from an oscillatory interaction between close-packed planes whose origin derives from the familiar Friedel oscillations. We shall find below that a similar oscillatory interaction associated with the interfaces of a metallic superlattice can lead to unusual stacking sequences for these compositionally inhomogeneous systems as well.

We discuss our results in the context of the tight-binding model of a metal. This choice contrasts with the nearly-free-electron pseudopotential approach adopted in the earlier bulk investigations but is particulary well suited for present purposes. There are three reasons for this. First, we wish to emphasize explicitly that the phenomenon of Friedel oscillations is not limited to the case of nearly free electrons. Indeed, they arise merely because a metal can only imperfectly screen out an external perturbation. Second, the tight-binding model is more appropriate to a discussion of the transition metals which constitute the principal components of most metallic superlattices. Finally, the geometrical mismatch between a spherical pseudopotential and a planar compositional interface leads to expressions that cannot be evaluated easily analytically. It is important to have some firm analytic results for this problem because it is impossible to search numerically for the ground-state stacking structure of a particular superlattice from the (formally) infinite number of conceivable polytypes.

Consider first the case of a single stacking fault in an otherwise perfect fcc bulk metal. That is, the crystal structure is . . . *ccccchcccc* . . . or . . . *ABCABCBACBA* . . . . If we employ the simplest conceivable tight-binding model (a single *s* state per site with on-site energy *E* and nearest-neighbor hopping integral V_1) this structure actually is degenerate in energy with the ideal fcc stacking.[8] However, we can generalize the model and add a longer-range interaction V_2 that couples the two planes on either side of the defect layer. The V_2 interaction is dominated by a single *B—B* bond in the defect *BCB* sequence whereas the dominant interaction in the fcc *BCA* sequence involves three pairs of *A—B* bonds at a slightly greater distance. The stacking fault now can be distinguished energetically from the perfect crystal. We denote the *difference* in V_2 between these two cases as ΔV_2.

The change in the total energy of any stacking sequence (relative to pure fcc) due to a finite value of ΔV_2 is given by[9]

$$\Delta E = -\frac{2}{\pi}\int_{-\infty}^{E_F} \mathrm{Im}\,\mathrm{Tr}\ln(1-G\Delta V_2)dE \;. \qquad (1)$$

In this expression, $G=(E-H)^{-1}$ is the one-electron Green's function of the perfect crystal. Since ΔV_2 generally is very small compared to V_1 it is sufficient to evaluate Eq. (1) within perturbation theory. Accordingly, to first order in ΔV_2, a layer sequence that contains N stacking faults contributes $\Delta E = N\mu_b$, which defines the bulk defect chemical potential, μ_b. Similarly, the term in Eq. (1) proportional to $\Delta V_2(i)\Delta V_2(j)$ gives the interaction energy between two stacking faults located at planes i and j. A detailed calculation[10] shows that this defect-defect interaction energy is given by

$$V(z) = (\Delta V_2)^2 A(E_F)\frac{\sin\{2z\cos^{-1}[(E_F)/(6V_1)+1]\}}{z^2} \;, \qquad (2)$$

where $z = |i-j|$ is the magnitude of the separation between stacking faults (assumed to be large) and $A(E_F)$ is a slowly varying function of the band occupancy. This function exhibits the same type of dependence on z as one finds in the analogous nearly-free-electron bulk case.[6]

Now imagine a *bicrystal* formed from two semi-infinite metals joined at a single compositional interface parallel to the close-packed planes. Intuitively, we expect the defect chemical potential to become position dependent due to the loss of translational invariance. To be more precise, we require the Green's function appropriate to such an interface for use in Eq. (1). This has been worked out by Yaniv[11] and, for our purposes, is characterized by a single parameter ΔF that describes the difference between the two metals. ΔF can stand for a difference in bandwidths, band fillings, interfacial bonding, or a combination of these.[12] We now place a stacking fault at a distance d from the interface and compute the energy change to first order in ΔF and ΔV_2. In the asymptotic limit ($d \gg 1$) we find

$$\mu(d) = \mu_b + \Delta F\Delta V_2 B(E_F) \times \frac{\sin\{2d\cos^{-1}[(E_F)/(6V_1)+1]+\delta\}}{d^2} \;. \qquad (3)$$

The phase shift δ depends in detail on the precise contributions to ΔF. Nevertheless, independent of the details, the key point is that the bicrystal interface introduces a Friedel-like oscillatory modulation to the bulk stacking-fault chemical potential. Equation (3) is valid for $-12V_1 < E_F < 0$ so one sees that there is a considerable variation in the modulation wavelength as the band fills.[13] To see its effect on the stacking structure, we consider several limiting cases (see Fig. 1).

Suppose that ΔF is large compared to both μ_b and ΔV_2. To first order in ΔV_2, the near-interface region (I) will exhibit stacking faults at every atomic plane where $\mu(d) < 0$. This case is shown in Fig. 1(b). As one moves away from the compositional boundary, the modulation amplitude drops off and a region (II) is encountered where the interface influence is comparable to the bulk defect-defect interaction [Eq. (2)]. As an example, suppose that $\mu(d)$ favors . . . *cchhcchhcc* . . . but the stacking fault interaction is repulsive at nearest-neighbor distances. In that case, a single-defect compromise structure, . . . *ccchccchcc* . . . may result as shown in Fig. 1(c). At sufficiently great distance from the interface, $V(z)$ dominates the problem and the structure must adopt the bulk stacking sequence. There is no problem if this happens to be fcc or hcp. However, suppose the bulk phase is a long-period polytype such as hcc. The broken translational invariance now becomes manifest and the interface will tend to place one of the h planes at a (shallow) minimum of the oscillatory chemical potential near the edge of the bulk-dominated region (III). It is easy to see that the other limiting cases do not introduce any new physics. If ΔF is of the order of ΔV_2, region I disappears and region II extends up to the interface. Similarly, if $\Delta F \ll \Delta V_2$, only region III exists.

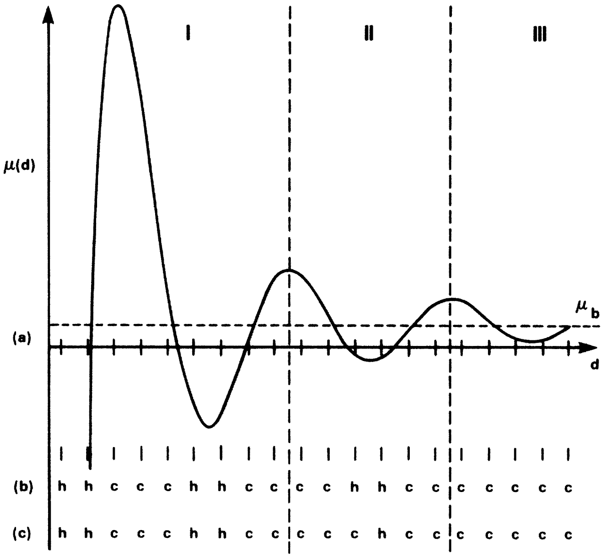

FIG. 1. (a) Chemical potential for an h stacking fault $\mu(d)$ as a function of distance d from a bimetallic interface. The horizontal axis is ruled in units of the interplanar distance. (b) Predicted stacking sequence based on $\mu(d)$ alone. (c) Predicted stacking sequence including the effect of defect-defect interactions.

We turn now to the case of a system that consists of a sequence of bimetallic interfaces, i.e., a superlattice. The atomic planes within each compositional layer feel the effect of two oscillatory potentials—one from each bounding interface. For large superlattice-modulation wavelength, i.e., thick layers, one expects stacking structures of the sort discussed above near each interface with the bulk structure in between. Again, if the bulk favors fcc or hcp, this completes the story. However, if the bulk structure is a long-period polytype, *both* interfaces will seek to lock it in, as above. A competition develops if these two alignments do not coincide. There are two possibilities. On the one hand, the bulk structure can align properly with one or neither interface and simply pay the mismatch energy cost. On the other hand, the incompatibility of the bulk phase with the boundary conditions set by the two interfaces (at the edge of their respective regions III) amounts to a demand that the *mean* distance between stacking faults l differ from its normal bulk value. However, one can always find *some* polytype that exhibits the required value of l. The superlattice will adopt this new stacking sequence in the overlapping region III if the energy difference between the new structure and the original bulk polytype is small compared to the aforementioned mismatch cost (see Fig. 2).

For short-period superlattices, the oscillatory contributions from the two interfaces must be superposed. Their relative phase obviously varies as the compositional layer thickness varies. If the two are *out* of phase, destructive interference occurs and the bulk structures should predominate except very near the interface. By contrast, if the two modulations are *in* phase, a stacking structure will be observed that bears no obvious relationship to the bulk phases (as in region I above). In particular, in the extreme limit when a compositional layer thickness is less than the oscillatory Friedel wavelength, a stacking fault can occur on every atomic plane; one converts an entire layer of fcc to hcp, or vice versa. This is one possible explanation for the stacking transition observed in thin Ru-Ir superlattices by Cunningham and Flynn.[3]

Finally, we wish to note two additional physical effects (absent from the present model) that can affect close-packed stacking configurations: elastic distortions and charge transfer. The influence of the former is treated in detail in Ref. 7. As for the latter, it is clear that charge must flow at the interface of two dissimilar metals. In general, the ensuing dipole layer formation leads to very small changes in band occupancy (even for the most extreme case of a metallic "superlattice"—a bulk alloy[14]). Nonetheless, the effect may be crucial in thin layers if μ_b already is very near zero in the bulk, i.e., near an fcc-hcp phase boundary. In that case, even small superlattice-induced changes in "valence" can drastically change the stacking sequence. Interestingly, a glance at a structural periodic table[15] reveals that Ru and Ir appear to straddle just such a phase boundary.

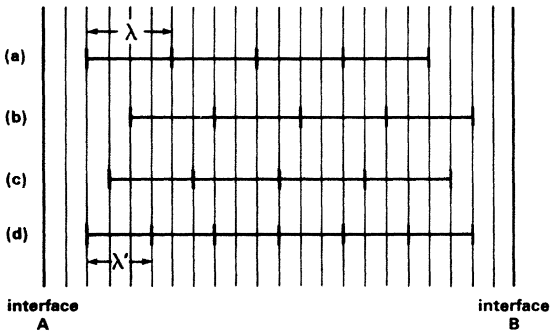

FIG. 2. Fate of a long-period polytype structure (λ is the stacking unit cell repeat length in the bulk) confined to a superlattice where the interfaces favor different alignments. (a) Bulk structure survives and aligns with interface A, (b) bulk structure survives and aligns with interface B, (c) bulk structure survives but aligns with neither interface, (d) stacking structure converts to a new polytype (λ') to accommodate alignment with both interfaces. Light vertical lines denote lattice planes.

In this Communication we have tried to show that some rather subtle structural effects can occur when junctions are fabricated from two close-packed metals—good candidates for single-crystal superlattice growth with sharp compositional interfaces. A simple tight-binding model is sufficient to reveal that the ubiquitous Friedel oscillations can determine the close-packed layer sequences in such materials. Compositional interfaces enhance stacking fault formation and, in some cases, can lead to entirely unexpected structures. It is hoped that these considerations will be useful to experimentalists trying to interpret x-ray diffraction data and theorists with an interest in the fundamental physics of superlattices.

We thank Robijn Bruinsma for helpful discussions at an early stage of this work and David Froelich for providing us with a plot of the density of states for our model.

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[9] See, for example, T. L. Einstein and J. R. Schrieffer, Phys. Rev. B **7**, 3629 (1973).

[10] The details of the calculation are tedious and unenlightening; we plan to publish them elsewhere.

[11] A. Yaniv, Phys. Rev. B **17**, 3904 (1978).

[12] Yaniv's Green's function depends on these various physical quantities in a complex manner. However, if one expands his results to lowest order, we find similar behavior for each of them.

[13] The band of our tight-binding model actually extends from $-12V_1$ to $+4V_1$. For $0 < E_F < 4V_1$ we find a more complex analytic result that replaces Eq. (3) although the qualitative behavior is similar. For details, see Ref. 9.

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[15] See, for example, H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).