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The uniaxially aperiodic structure of a thin Cu film on fivefold *i*-Al–Pd–Mn

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Abstract
A thin film of copper on the fivefold surface of Al–Pd–Mn forms a structure that is uniaxially commensurate with the aperiodic structure of the substrate. This structure has been analyzed using low-energy electron diffraction and is found to consist of a vicinal surface of a body-centered tetragonal (bct) (100) structure. This bct(100) structure has lattice parameters of $a = 2.88$ Å, $b = 2.55$ Å and $c = 2.88$ Å, with the vicinal surface making an angle α of 13.28° relative to the a–b plane. This structure provides an explanation for the delayed ordering observed during the growth of the film. Simple conditions are derived for which the growth of ordered one-dimensionally quasiperiodic thin films on quasicrystals may be favorable. This finding is relevant to the use of quasicrystals as a means of matching interfaces in thin film systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

This paper was written for this *Journal of Physics: Condensed Matter* special issue to honor the career of Richard Palmer, formerly the publisher of this journal. The study of the properties of quasicrystal surfaces represents a field that developed entirely within the era of Richard Palmer's reign at *Journal of Physics: Condensed Matter*. Indeed, Richard was already slaving away at IOP Publishing when quasicrystals were first reported in 1984 [1]. The development of low-energy electron diffraction for the characterization of quasicrystal surfaces [2] is even more recent, with the first dynamical low-energy electron diffraction (LEED) paper on quasicrystals published in 1997 [3]. The properties of quasicrystalline interfaces have received considerable attention recently and are the subject of a special section in *Journal of Physics: Condensed Matter*, published in August 2008 [4–8]. Quasicrystal interfaces and the use of dynamical LEED to characterize them are the subjects of this paper, which examines the growth of a copper film on the Al–Pd–Mn quasicrystal surface.

The growth of Cu on the fivefold surface of *i*-Al–Pd–Mn has many curious features [9, 10]. It was observed in scanning tunneling microscopy (STM) experiments that Cu initially forms small, flat and mostly rounded islands. These islands coalesce into a connected film, which grows with a clear layer-like structure, having curved boundaries. As the film grows to several layers thick, these curved boundaries gradually become straight, and well-defined ridges become evident on the top of the film, as shown in figure 1. During the first few layers of this growth, the LEED pattern from the clean Al–Pd–Mn surface gradually diminishes, with a new LEED pattern emerging after about four monolayers of Cu have been deposited on the surface. LEED patterns from the clean surface and from a film of five layers are shown in figure 2.

One of the curious features of this growth concerns the 'delayed' ordering of the film. There is no apparent ordering of the Cu in the film at coverages up to a few layers, i.e. there are no diffraction peaks, and the boundaries of the film are rounded, as if determined mainly by the intra-layer interactions. There is little if any long-range commensuration of the Cu film with the substrate at low coverages. However, for an equivalent coverage of about 4 ML of Cu, well-defined ridges on the Cu film are evident and they correspond exactly to the substrate Fibonacci grid. Thus, while the substrate structure appears to have little effect on the ordering of the film up to a few layers, it exerts a marked effect on the film at thicknesses greater than about four layers. This aperiodic structure persists

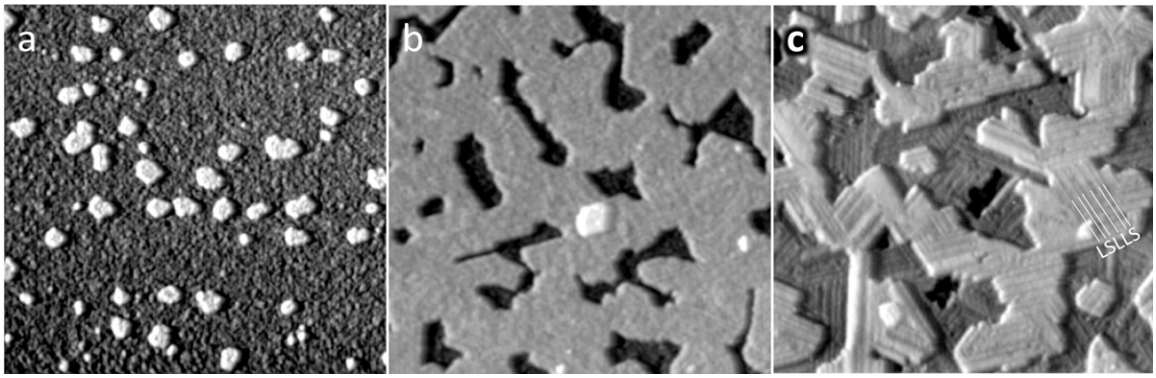

Figure 1. (a) 500 Å × 500 Å STM image of 0.09 ML of Cu. (b) 500 Å × 500 Å STM image of 3.8 ML of Cu. (c) 700 Å × 700 Å STM image of 5.5 ML of Cu. The coverages refer to monolayer equivalents of Cu, determined by calibrating the Cu flux by STM observation of successive fractional layer coverages. An example of the LSLLS row structure is indicated in (c).

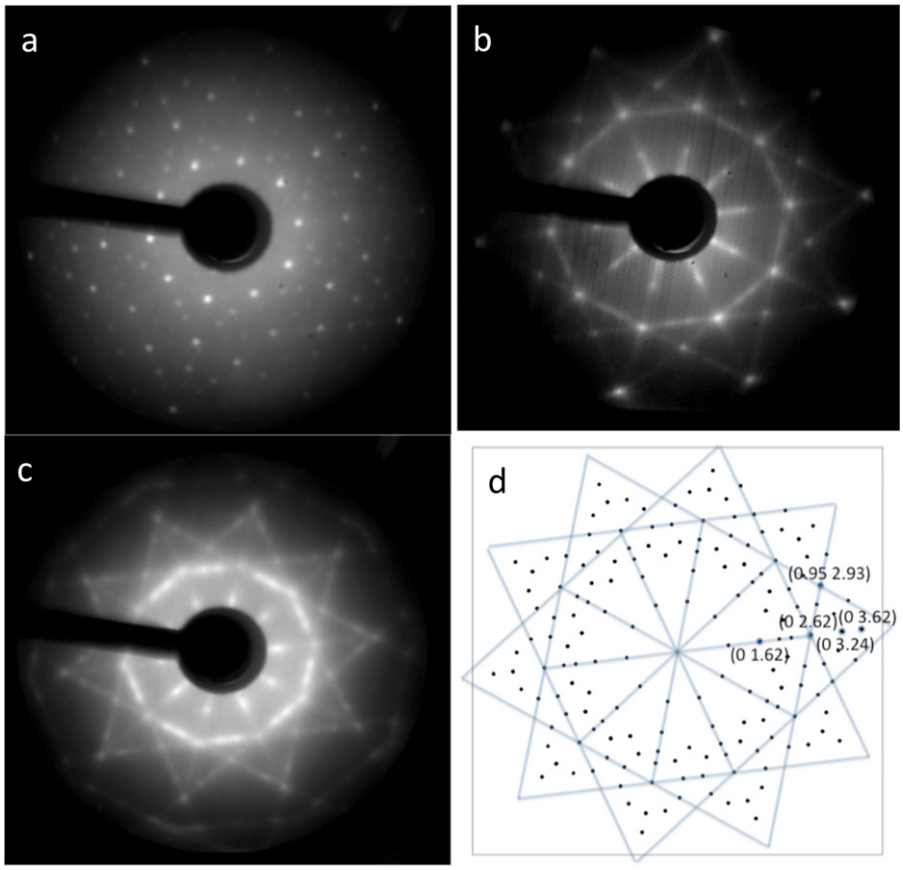

Figure 2. LEED patterns from (a) the clean Al–Pd–Mn surface at 112 eV, a five-layer Cu film on AlPdMn at (b) 112 eV and (c) 177 eV and (d) a schematic diagram showing the beam indices used for this analysis. The temperature of the sample was 85 K.

up to an equivalent coverage of at least 20 ML [9, 10]. Such a long-range effect of the substrate potential is atypical in metal film growth.

The influence of the substrate on the film structure is evident in the LEED patterns shown in figure 2. While the Cu film LEED pattern shown in figure 2(b) looks quite different from the clean surface LEED pattern shown in figure 2(a), the locations of the main diffraction spots are identical. There are important differences in the LEED patterns, however. First, the LEED pattern from the Cu film has almost complete tenfold symmetry, whereas that from the clean surface has clear fivefold symmetry. In addition, the LEED pattern from the film is streaked along certain symmetry directions. These streaks are spaced periodically [10], with a separation of 2.48 ± 0.03 Å^{-1}. This corresponds to a real-space separation of 2.53 ± 0.03 Å, which is near the Cu–Cu spacing in bulk Cu of 2.55 Å. The identical positions of the diffraction spots in LEED patterns from the clean surface and the Cu film indicate

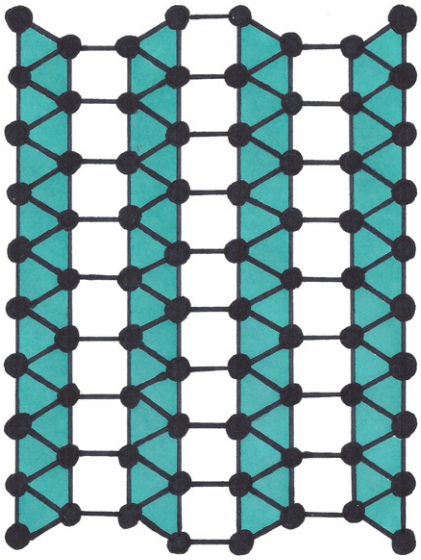

Figure 3. An example of an Archimedes tiling structure consisting of alternate rows of equilateral triangles and squares.

that the aperiodicity of the Cu film is the same as the clean surface, meaning that it corresponds to the same L and S Fibonacci distances, or some τ inflation of them. The step height within domains of the Cu film was measured in the STM experiment to be 1.9 Å [9].

By fitting the measured parameters from both the STM and LEED experiments, it was possible to derive a basic structure model that exhibits all of the properties described above [9]. This model consists of five rotated domains, having a periodicity of 2.53 Å in one direction and the substrate Fibonacci structure in the perpendicular direction. The Fourier transform of such a model is consistent with the observed LEED patterns [10]. However, the atomistic structure within this model cannot be determined from the spot locations in the LEED patterns alone. For this, the spot intensities must be analyzed. An earlier LEED intensity analysis of this surface considered atomistic models based on fcc(100), fcc(111), fcc(110) and a stepped body-centered tetragonal (bct) surface. Some agreement was found for film structures based on the fcc(100) domains, but the result was not entirely satisfactory because it involved unphysically close Cu atoms [11]. The same is true of a similar model that was used to fit MEIS data from the same film [12]. Aside from the unphysical parameters, this model also provided no insight into the unusual growth and ordering of this film.

In the study reported here, we have extended the dynamical LEED analysis to different models, including the Archimedes tiling type structures recently observed in two-dimensional colloidal suspensions [13, 14] and we have revisited models based on vicinal surfaces. We find that the best fit is for a model based on a vicinal bct structure. Aside from the fact that it produces a better fit to the experimental data, a vicinal model is more physically sound than the best-fit flat surface models because (1) the nearest-neighbor distances are more reasonable, (2) it offers an explanation for the observed delayed ordering during film growth and (3) it offers an explanation for the registry of the film with the substrate. The calculational procedures are the same as before [11], based on the periodic approximant method that has been described elsewhere [15].

Table 1. Pendry R factors for the tested models, including those in [11].

Model	R factor
Fcc(100)	0.32–0.47
Fcc(110)	0.81–0.92
Fcc(111)	0.87–0.93
Archimedes	0.47–0.53
Vicinal bct(100)	0.26

2. Archimedean tiling models

A recent study of two-dimensional colloidal monolayers found that, under appropriate conditions where a fivefold quasicrystalline ordering force is applied to the monolayer, Archimedean tiling structures are observed [13]. An example of an Archimedes tiling structure is shown in figure 3. This structure is composed of alternating rows of square and triangular tiles. Such a model can be adapted to the Cu film structure by inserting additional rows of triangles to create a locally aperiodic structure. Diagrams of the Archimedean tiling structure models tested in this analysis are shown in figure 4. They were constructed using periodic LSLSL unit cells. In all models, the L strip consisted of three rows of copper and the S strip consisted of two rows of copper. Within this basic model, the copper layers can be stacked in three different ways: ABAB$\cdots$ (model a) or AB′AB′$\cdots$ (model b) or AAAA$\cdots$ (model c), where the B is shifted half of the Cu–Cu distance with respect to the A layer in the x direction and B′ is shifted the same amount, but in the y direction.

In the first set of calculations, the in-plane Cu–Cu distance was 2.5527 for both x and y directions, giving $L = 6.97$ Å and $S = 4.76$ Å. The R factors for these structures after relaxing two top layers (27 free parameters) were 0.53 (model A), 0.56 (model B) and 0.48 (model C). The average Cu–Cu distance across the rows was then increased to achieve the longer and more realistic L and S spacings of 7.3 and 4.5 Å. The R factors after relaxation were 0.52, 0.47 and 0.53, respectively, for the three stacking models shown in figure 4. These R factors are not as good as for the fcc(100) models studied previously (see table 1).

3. Vicinal surface models

It is well known that surfaces of periodic crystals may show aperiodicity in one dimension by making a cut through the crystal at an appropriate angle [16]. For these surfaces, the surface orientation, the terrace length and the step height are related to each other in the following way.

If we consider a crystal that is cut to produce terraces having two widths a_1 and a_2, separated by monatomic steps having a height b, then for the surface to be aperiodic in one dimension, it must satisfy the condition, based on the drawing

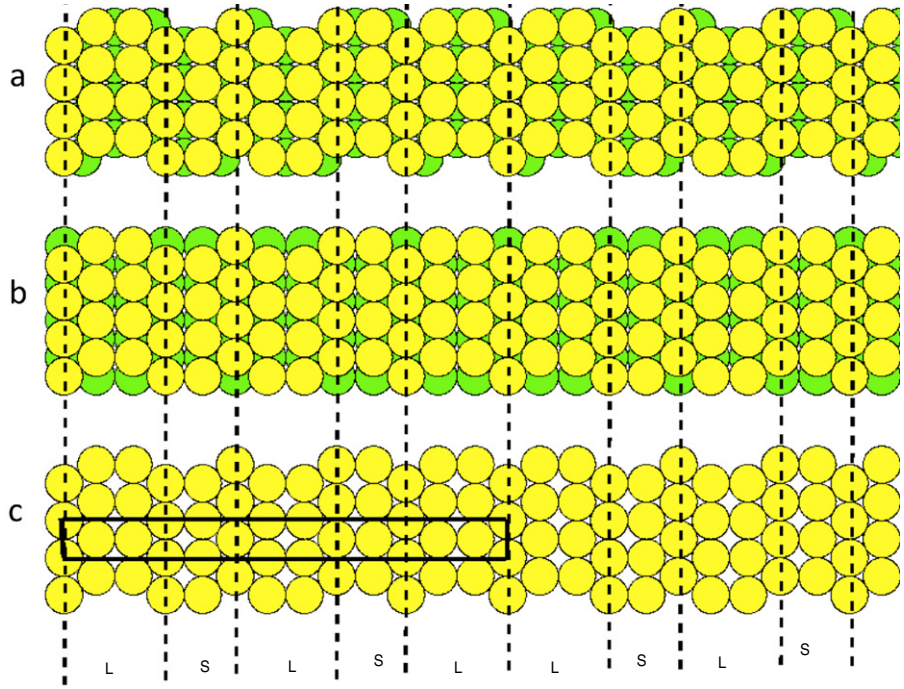

Figure 4. Top views of the three different stacking sequences for the Archimedes tiling structure models.

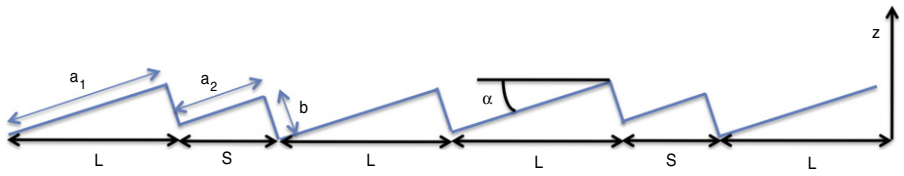

Figure 5. Vicinal surface model with terraces of a low-index surface along a_1 and a_2, and perpendicular steps along b, having an aperiodic array of steps. The angle α is calculated using equation (6).

in figure 5, that the lengths L and S are related by $L/S = \tau$, where τ is the golden mean.

The aperiodic surface is perpendicular to the z direction, as shown. L and S can be calculated in terms of a_1, a_2 and b:

$$L = a_1 \cos\alpha + b \sin\alpha \tag{1}$$

$$S = a_2 \cos\alpha + b \sin\alpha. \tag{2}$$

The condition that $L = \tau S$ gives

$$a_1 \cos\alpha + b \sin\alpha = \tau(a_2 \cos\alpha + b \sin\alpha). \tag{3}$$

In order to evaluate this, we make use of the fact that, in a Fibonacci series, the long termination L occurs τ times as frequently as the short termination S. Therefore, the average terrace length is

$$\langle a \rangle = \frac{\tau a_1 + a_2}{\tau + 1} \tag{4}$$

and the following condition ensures that the surface normal is along z:

$$\langle a \rangle \sin\alpha = b \cos\alpha. \tag{5}$$

From equations (4) and (5), the step height dependence on a_1 and a_2 can be calculated as follows:

$$\alpha = \arcsin\left(\frac{b\tau^2}{\sqrt{(\tau a_1 + a_2)^2 + b^2\tau^4}}\right). \tag{6}$$

Insertion of (6) into equation (3) gives the following expression for the step height:

$$b = \sqrt{a_1 a_1 - a_2 a_2 - a_1 a_2}. \tag{7}$$

From these considerations, we can derive the following conditions under which the growth of ordered metal layers with one-dimensionally quasiperiodic surfaces may be favored:

(1) The miscut angle with respect to a low-index surface is given by equation (6) and the step height obeys the relation (7). These conditions ensure that the surface is one-dimensionally quasiperiodic, with the long and short terrace lengths being related by the golden mean τ.
(2) The lengths L and S, as indicated in figure 5, are close to the characteristic lengths of the quasicrystal surface (which may be, for example, the distances of the Fibonacci grid connecting the pentagonal hollows of the fivefold symmetric surface of AlPdMn).
(3) The surface energy of the one-dimensionally quasiperiodic surface is low enough so that faceting is not energetically favorable.

In the following, we show that a stepped body-centered orthorhombic structure is a likely candidate for the Cu film

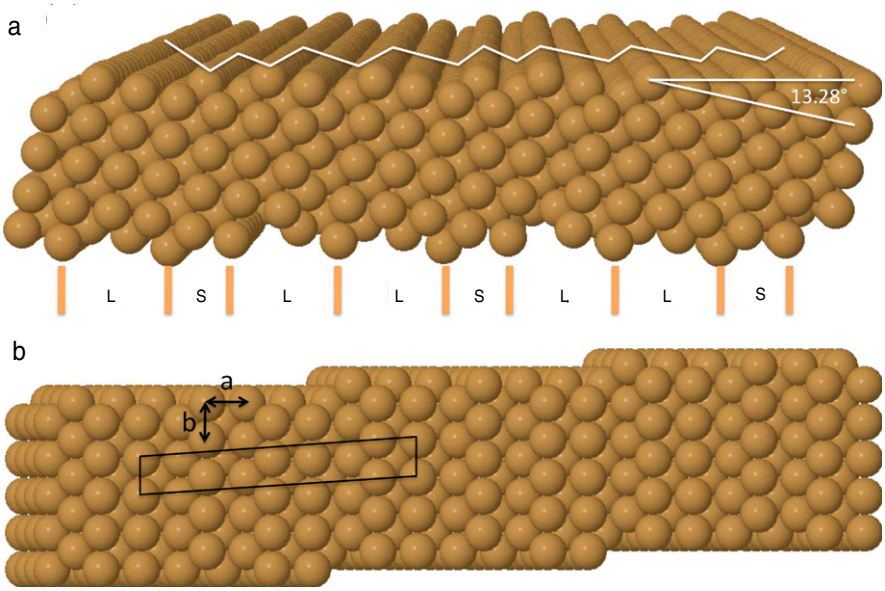

Figure 6. (a) Perspective side view of the vicinal body-centered orthorhombic LSL model, showing the L and S distances across the bottom and a schematic of the step structure at the top. (b) Top view of the stepped same model, showing the surface unit cell and the parameters a and b.

structure studied here. Metastable bcc Cu has been reported in the literature [17], as well as thin films of bcc Cu on Fe(100) [18] and Ag(100) [19] and body-centered tetragonal Cu on Au(100) [20] and Pd(100) [21]. The difference between orthorhombic, tetragonal and cubic is the number of sides that are equal: cubic has $a = b = c$, tetragonal has $a = b \neq c$, while orthorhombic has $a \neq b \neq c$. An example of the stepped orthorhombic model used in this calculation is shown in figure 6.

For the present case of Cu on AlPdMn, we need to find a stepped surface for which L and S are close to the characteristic distances on the AlPdMn surface, namely $L = 7.30$ Å and $S = 4.52$ Å. First of all, vicinal (100) surfaces can be ruled out as candidates for these structures. For these surfaces, the step height is equal to $a/\mathrm{sqrt}(2)$, and it is easy to see that a stepped fcc(100) surface cannot fulfill the step height condition (7) for appropriate values of L and S. Considering a bcc(100) lattice, the lengths of the long and short terraces are given by $L = 2.5a$ and $S = 1.5a$, respectively, with a corresponding to the nearest-neighbor distance on the bcc(100) surface. The step height of the bulk-terminated surface is $0.5a$, so that condition (7) is satisfied. From (6), we find that the angle with respect to the (100) plane is $\alpha = 13.28°$. Insertion of a nearest-neighbor distance 2.88 Å [20] into equation (1) gives $L = 7.34$ Å, which is close to the distance between the Fibonacci grid lines on the AlPdMn surface. In order to meet the condition set by the nearest-neighbor distance of 2.5 Å along the rows while maintaining a realistic density, a body-centered orthorhombic or body-centered tetragonal structure is a more likely candidate for this film.

In the structure shown, the unit cell represents an LSL unit of the Fibonacci sequence. The lattice parameters were varied during the analysis, as was the angle between the orthorhombic (100) plane and the surface plane, with the constraint that the L and S distances parallel to the surface must be 7.30 and 4.52 Å, respectively. The best-fit model has Cu–Cu spacings indicated as a and b in figure 6(b) of 2.88 Å and 2.55 Å, respectively. The third lattice parameter is also found to be 2.88 Å, making the structure body-centered tetragonal (bct) and the interlayer spacing perpendicular to the surface is 0.68 Å. During the analysis, the layers down to 8 Å are relaxed and the structural parameters parallel to the surface were optimized (41 free parameters), resulting in a final R factor of 0.26. There is a considerable amount of relaxation of the Cu atoms from the perfect bct structure. There are no specific trends for the relaxation of the surface planes, but rather a buckling of the surface atoms by an average of about 0.11 Å. The net effect of the buckling appears to enhance the step structure.

Figure 7 shows the experimental and fitted calculated spectra. Although the agreement for these spectra is good, the experimental spectra are systematically smoother than the calculated ones. This is likely due to disorder in the structure, some of which is evident in the STM images. In order to model the disorder, a larger-than-typical imaginary term was used in the scattering potential (−10 eV); however, this does not fully account for the difference. It is possible that the structure we have found is a local minimum in the R factor rather than the true minimum and further studies may elucidate this. However, based on the factors discussed below, we believe that the basic features of the model are correct and that the vicinal model provides a good description of this film.

4. Discussion

The Archimedes tiling structure models tested here represent interesting and plausible structures for a two-dimensional layer under the influence of a fivefold potential. However, when applied to this Cu film, the agreement is not as good as other

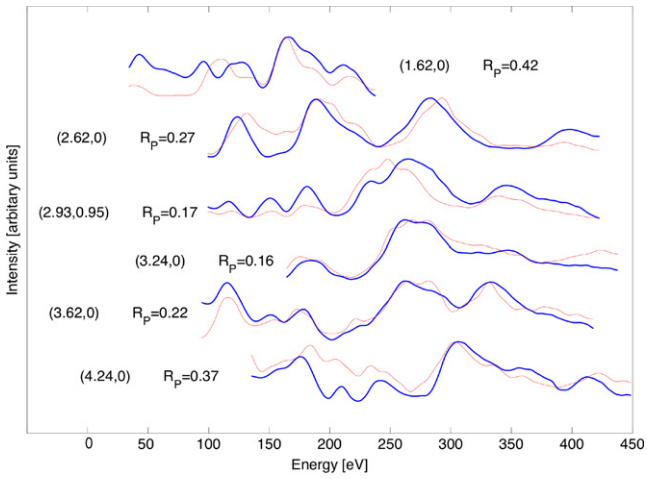

Figure 7. Best-fit experimental (bold) and calculated LEED spectra using the stepped bct model. Individual beam *R* factors are noted.

models. A difficulty with this model, which is also true for the low-index fcc models, is that it offers no insight into the delayed ordering observed in both the STM and LEED.

The vicinal structures, on the other hand, require several layers to form before their crystal structure is evident. The observation of small islands of Cu, followed by connected islands, suggests that the initial Cu islands nucleate at particular sites on the surface. The STM clearly shows that the subsequent growth of the film is layer by layer. The lack of diffraction spots after deposition of one or two layers indicates a lack of long-range order in this film at these coverages. At a critical coverage, which appears to be about four layers, the film orders. Because the structure of the Cu film is uniaxially commensurate with the substrate, the whole film must be completely ordered. In other words, the film does not consist of ordered layers on top of the disordered layers, but of all ordered layers. Otherwise, the substrate would not be able to exert an ordering influence on the outer layers.

The nature of the ordering field provided by the substrate is likely an aligning field that is created by parallel lines of lower average potential energy at the surface. The adsorption potential for Cu on the Al–Pd–Mn surface is not known, but its form is likely to be similar to that calculated for Xe [22] or Al [23] on Al–Ni–Co using simple phenomenological models. On that surface, the calculated adsorption potentials for Xe and Al have rows of lower potential energy that facilitate the periodic ordering of Xe or Al. In these cases, too, there appears to be a critical coverage required before the periodic ordering occurs.

Unlike those cases, however, the Cu film requires several layers before ordering occurs. This is likely because it cannot crystallize into the vicinal bct structure until several layers are present, i.e. the structure cannot exist as bct until several layers exist. When the critical thickness is achieved, the substrate field imposes this particular vicinal surface because it has the correct L and S spacings.

Figure 8 shows an STM image of a small part of a Cu film, showing several layers of the Cu film. The ridges observed in the images are continuous across the steps, but there is a small lateral offset from one terrace to the next. This offset is also present across steps (=1.73 Å) in the vicinal bct model structure, as shown in figure 8(c). A similar offset is also present in the Archimedes model shown in figure 4(a), but not the ones shown in figures 4(b) and (c). Offsets are also present in the fcc(100) models considered earlier [11].

We note that the above considerations about vicinal planes can be extended to other systems, such as Al on AlPdMn. Growth of Al at temperatures of about 300 K leads to the formation of Al fcc nanocrystals with their growth planes tilted by 37° with respect to the substrate plane [23, 24]. Neglecting interdiffusion and reconstruction, the Al structure at the interface may be modeled by a stepped fcc(110) plane, with the steps along the $[\bar{1}10]$ direction perpendicular to the close-packed rows. The terrace lengths are $2.5a$ and $1.5a$ and a step height of $0.5a$. The miscut angle with respect to the (110) surface is $\alpha = 13.28°$. With the lattice constant for Al of $a = 2.86$ Å, the terrace length from equation (1) is 7.29 Å, again close to the characteristic L length of 7.38 Å. For this model, the (111) planes are tilted by 37.37° with respect to the surface plane, in agreement with the findings in [23, 24].

5. Conclusion

This LEED analysis shows that a vicinal body-centered tetragonal structure provides a better model for the observed aperiodic Cu film than various two-dimensional models. The best-fit result consists of a bct film with $a = 2.88$ Å,

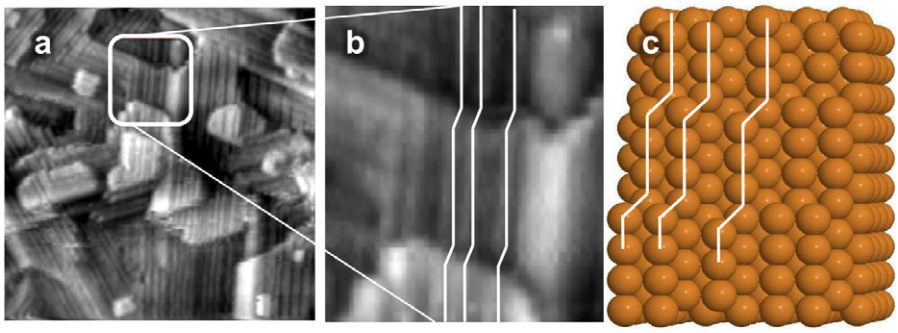

Figure 8. (a) 350 Å × 350 Å STM image of an 8.7-layer Cu film on Al–Pd–Mn. (b) Enlarged section of (a), showing the alignment of the rows across the steps. (c) Model bct structure, showing the same row offset at the steps as observed in (b).

$b = 2.55$ Å and $c = 2.88$ Å, with the surface at an angle of 13.28° relative to the a–b plane. This model provides a more plausible explanation for the observed delayed ordering of the film than is possible with two-dimensional models. We derived simple conditions under which the growth of ordered layers with quasiperiodic surfaces on quasicrystal surfaces may be favorable and it may be interesting to investigate whether other systems, for example bcc metals, form similar structures.

Acknowledgments

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