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J. Ledieu
University of Liverpool

J. T. Hoeft
University of Liverpool

D. E. Reid
University of Liverpool

J. A. Smerdon
University of Liverpool

R. D. Diehl
Pennsylvania State University

See next page for additional authors

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Copper adsorption on the fivefold Al$_{70}$Pd$_{21}$Mn$_9$ quasicrystal surface

J. Ledieu,* J. T. Hoeft, D. E. Reid, and J. A. Smerdon
Surface Science Research Centre and Department of Physics, The University of Liverpool, Liverpool L69 3BX, United Kingdom

R. D. Diehl and N. Ferralis
Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802, USA

T. A. Lograsso and A. R. Ross
Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA

R. McGrath
Surface Science Research Centre and Department of Physics, The University of Liverpool, Liverpool L69 3BX, United Kingdom

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Recently we reported the formation of a quasiperiodic Cu thin film on the fivefold icosahedral Al-Pd-Mn quasicrystal using scanning tunneling microscopy, low energy electron diffraction, and Auger electron spectroscopy. Here we provide details pertaining to the growth, stability, and structure of this film. Structural information has been gained by LEED measurements carried out at 85 K. Cu atoms are organized periodically with a nearest-neighbor distance of 2.5±0.1 Å along the aperiodically spaced rows. Above 8 ML spontaneous mass transport resulting in island formation has been observed by STM. These observations point to adatom processes being responsible for the formation of 3D features. Finally, flashing the multilayer film to 570 K results in the desorption or diffusion of Cu into the bulk and the formation of five domains of a periodic structure.

I. INTRODUCTION

Quasicrystals, which are examples of complex metallic alloys, have extended the horizons of crystallography. The aperiodic order, and “unusual” symmetries observed in these materials have put to the test fundamental rules of crystallography established over the last century. Consequently the definition of a crystal has been modified to incorporate quasicrystals. Among the large family of quasicrystals, the icosahedral Al-Pd-Mn phase has been the most studied and a model explaining its bulk structure has been proposed by Boudard et al. in 1992 and later refined by Yamamoto. The surface structure of this material has been identified and determined to be a termination of the bulk structure. The local atomic configuration [see Fig. 1(a)] is best described with pentagonal dark stars, pentagons and flowers. This significant step towards understanding the surface structure is the result of close collaboration between theory and experiment over recent years. Hard-sphere surface planes have been extracted from bulk models and compared to data from imaging techniques. These planes have been of importance in determining possible nucleation sites in recent adsorption experiments.

Substantial effort is now being put into using quasicrystal surfaces as growth templates. The goal is the formation of a single element quasiperiodic overlayer, i.e., an aperiodic system of reduced complexity and dimensionality. The formation and study of such systems should provide insight into the impact of aperiodicity on physical properties. To that end, adsorption of Al (Ref. 16) and Ag (Ref. 17) has been carried out on the fivefold Al-Pd-Mn surface. In the first study, five face-centered-cubic domains of Al are obtained. The [111] axes of the Al nanocrystals are aligned parallel to one of the threefold symmetry axes of the sample at an angle of 37.37° to the surface normal. In the second experiment, hexagonal nanocrystals are formed. They grow in five orientations, reflecting the symmetry of the underlying substrate. At 0.04 ML coverage, Al adsorption on the fivefold Al-Cu-Fe surface resulted in the formation of fivefold Al nanoclusters. The growth mode was characterized as pseudomorphic. Similarly Sb and Bi quasiperiodic monolayers on both i-Al-Pd-Mn and d-Al-Ni-Co were formed by Franke et al. Both elements have been deposited at 570 K followed by annealing to 820 K. Shimoda et al. reported the formation of a 10 Å thick binary Al-Au alloy layer exhibiting icosahedral symmetry.
This epitaxial film was obtained in the presence of predeposited In (Ref. 19).

We recently reported the formation of a quasiperiodic thin film by depositing Cu on the Al-Pd-Mn surface Fig. 1(a) at room temperature.20 Cu adsorption on such a surface is shown for three different coverages in Figs. 1(b)–1(d). At 0.08 ML, islands were observed. They appear isotropic in shape with a constant step height measured at 1.9±0.1 Å. The same layer-to-layer step height is maintained throughout the experiment independent of the coverage. At 5.5 ML, a new LEED pattern, generated by the Cu structure, is observed. The structure on the surface at this coverage is now described as an arrangement of 1D features aligned along the five principal directions of the quasicrystal substrate [Fig. 1(c)]. Copper is the only element present in the film as monitored by Auger spectroscopy. Between the lines, two spacings are measured, one at 4.5±0.2 Å (S) and the other at 7.3±0.3 Å (L). As shown in Ref. 20, S and L are ordered in a Fibonacci-type manner. As the coverage was increased, this row structure was preserved but islands got progressively smaller. This eventually generated incomplete layers as shown in Fig. 1(d). The LEED pattern present up to a 20 ML coverage started to degrade and finally vanished at 25 ML.

In this paper we extend the investigation of Cu deposition on Al-Pd-Mn using scanning tunnelling microscopy (STM), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). Section II contains experimental details. STM and LEED measurements at low temperature have been carried out and are presented in Sec. III A. At high coverage (>8 ML) we have recorded in real time the spontaneous growth of islands. This is presented in Sec. III B. When annealed to 570 K for a short time Cu desorption or diffusion occurs and the quasiperiodic film transforms to periodic domains. This is analyzed in Sec. III C. Finally, these results are discussed in Sec. IV.

II. EXPERIMENTAL DETAILS

The sample used in this experiment (Al70Pd21Mn9) was grown at the Ames laboratory using the Bridgman method. After alignment with back reflection Laue x-ray diffraction the sample was cut perpendicular to its fivefold axis. In order to start with a macroscopically mirrorlike finish the sample was polished down to 1/4 µm diamond paste. This has also been found to improve the overall surface preparation6 in comparison with polishing using only 6 and 1 µm diamond paste. After insertion in ultrahigh vacuum the sample preparation consists of cycles of sputtering at a grazing incidence angle (90 minutes for the first two cycles and then 45 minutes) and annealing to 940 K for a total of 20 hours. The purity of argon gas used during the ion bombardment process was checked by a quadrupole mass spectrometer. The temperature was measured by an infrared optical pyrometer (emissivity set to 0.35). The level of contamination (mainly oxygen and carbon), and Cu coverage, was monitored by AES and the overall structure at the surface was assessed by LEED. The local atomic arrangement was probed by a Omicron variable temperature STM (VT-STM). Measurements were conducted at room temperature and at 25 K. The Cu source used in the experiment consists of a tantalum wire (0.125 mm) tightly twisted around a rod of copper (99.9%, oxygen free). The source was thoroughly degassed until Cu wet the Ta wire. Identical dosage conditions were used throughout the experiment with the flux of the source measured at 4.5×10−2 monolayer (ML) s−1.

In a separate chamber (Penn State University) LEED measurements at low temperature were carried out using a conventional VG 3-grid rear-view LEED system. The data were collected using a CCD camera interfaced to a PC equipped with a frame grabber board. The Al-Pd-Mn sample was clamped onto a sample holder that was equipped with an electron beam heater and attached by a copper braid to a liquid helium open-cycle refrigerator. The Al-Pd-Mn was prepared in a similar manner to the one described above. The Cu film was dosed onto the surface using the established method (sample was at 308 K during dosing) and its coverage was estimated by a comparison of Auger electron spectra and LEED patterns to those established in earlier experiments. The Cu coverage estimated for these experiments is six monolayers. The LEED data were acquired from this surface for a surface temperature of 85 K.

III. RESULTS

A. STM and LEED investigation at low temperature

As reported in Ref. 20, Cu adsorption on the Al-Pd-Mn surface leads to the formation of a quasiperiodic thin film. The structure has been investigated using STM. However, despite the use of different sharp tips and varying the tunnelling conditions, it was not possible to obtain atomic resolution within the Cu rows at room temperature. This could be explained by the atomic motion being too pronounced along the rows. For that reason, the experiment was also carried out at a lower temperature to reduce atomic vibrations. The pseudomorphic Cu thin film was prepared at room temperature and then cooled down to 25 K. The Cu rows arranged in a Fibonacci manner were still present but unfortunately atomic resolution was still not attained within the Cu rows at that temperature. A delocalized charge density along the rows is the most probable explanation of the lack of atomic resolution.

Although no more structural information could be gained using STM, LEED patterns recorded at low temperature reveal details on the structure along the Cu rows. Figure 2(a) shows the LEED pattern from the Cu film for an incident beam energy of 335 eV. The intensity streaks evident in this pattern are periodically spaced and are present in five directions rotated by multiples of 72°. The low-order streaks can be seen more clearly in Fig. 2(b), which shows the LEED pattern at 169 eV. While the streaks themselves are periodic, the primary spots within the streaks are quasiperiodically spaced. The streaks are parallel to the principal axes of the quasicrystal surface, a fact which can be verified by comparing the LEED pattern in Fig. 2(b) to that from the clean surface at the same energy, shown in Fig. 2(c). The presence of such streaks indicates that the Cu structure is periodic perpendicular to the direction of the quasiperiodic ordering, i.e., along the rows observed in the STM images. This cor-
The diffraction spot indicated on Fig. 2 = 2.5 ± 0.1 Å. This period is essentially the same as the therefore the periodic spacing along the rows is 2

Using this to calibrate the Cu LEED pattern, the momentum transfer of the periodic streaks is found to be 2.48 Å−1, and as many rows as would fit (without distortion) were included in the model. The five rotational domains of this structure are shown in Fig. 2(d), and its FT is shown in Fig. 2(e). This FT is very similar to the observed LEED pattern in Fig. 2(b).

The details of the structure model used are shown in Fig. 2(f). The structure consists of rows of periodically spaced (2.5 Å) atoms. These rows are then placed on a Fibonacci sequence having spacings of 4.5 Å and 7.3 Å. Additional rows are added to fill in the structure, creating parallel “panels” of a relatively close-packed Cu structure, spaced according to the Fibonacci sequence. Because the interlayer spacing measured using STM (1.9 ± 0.1 Å) is consistent with the interlayer spacing expected for the (001) surface (1.81 Å) it was assumed that this distance is essentially unperturbed from (001), and that the density of the Cu must be close to the bulk value. The result is Cu rows that are separated by about 2.5 Å in each panel. There is no real need (nor evidence) for this distance to be the same in all panels, and it is likely to be somewhat different in the long and short panels. For clarity, we have left some open areas between the panels in this structure, although these areas are likely to be filled in the real structure.

A detailed analysis of the intensity profiles along the streaks indicates that the locations of intensity peaks along the streaks are the same as those from the clean surface. Perhaps more importantly, there are no peaks evident along these streaks. In particular there is no appreciable intensity at locations at or near the momentum transfers that would be expected for a (001) or (111) surface. Therefore, it appears that the quasiaperiodicity dominates the Cu structure along the directions perpendicular to the rows. This is consistent with the STM observations. Therefore, the film should be regarded as higher-order commensurate in the direction perpendicular to the rows, and as being at the strong domain wall limit (as opposed to a weakly modulated structure). We note that in the FT simulations of the diffraction patterns, intensity was observed at or near the locations of (001) reflections [for the models based on (001)] unless the panel-to-panel registry along (110) was disordered, as shown in Fig. 2(f). We feel that this provides some evidence that the panels

### Table I. Interlayer spacings for Cu (111), (001), and (110) faces.

<table>
<thead>
<tr>
<th>Cu face</th>
<th>dz (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>2.08</td>
</tr>
<tr>
<td>(001)</td>
<td>1.80</td>
</tr>
<tr>
<td>(110)</td>
<td>1.27</td>
</tr>
</tbody>
</table>

How to place the atom rows relative to each other, we noted that the step height measured by STM is about 1.9 Å, and the Cu atoms are essentially close-packed along the rows. The most likely arrangement having these two parameters is a (001) arrangement of atoms. Note that the interlayer spacings for (110) and (111) are not as close to the measured value of 1.9 Å (see Table I).
are not necessarily aligned, and indeed, it seems to us more likely that the panels nucleate independently at sites along the substrate rows, and therefore the panel-to-panel registry is dictated by the substrate structure. This cannot be proved conclusively from the LEED, although we note that it is consistent with the observation that peak intensities occur only at momentum transfers consistent with the substrate structure.

It should be emphasized that it is not possible from the LEED pattern to distinguish various structure models, and the model shown in Fig. 2(f) is not the only model that will produce a FT similar to that shown in Fig. 2(e). An alternative model would be based on a (111) plane, with the close-pack direction along the rows. In this case, the row-row order would be ABAB (instead of AAAA) in the horizontal direction in Fig. 2(f). Such a model is consistent with the LEED pattern, but is less consistent with the interlayer spacing as measured by STM. Again, we note that no intensities were observed at locations expected for either (111) or (001) surfaces.

**B. Spontaneous island formation**

At high coverage (>8 ML) spontaneous mass transport has been recorded by STM. An example is shown in Fig. 3 where four consecutive STM images of the same area recorded over a 5 minute period at room temperature are presented. Although the step edges appear unchanged (region 1 in the figure), the morphology of the film is evolving considerably as indicated by the white arrow. If one compares the height at that particular point between Figs. 3(a) and 3(d), the difference is striking. The arrow on Fig. 3(d) points to a stacking of islands into a needlelike shape not present at the beginning of the scans. The second observation is the increase between Figs. 3(a) and 3(d) in the number of Cu layers visible in region 2. This indicates an important mass transport between region 2 (getting deeper) and the region marked by the white arrow (getting higher). Considering the tunneling conditions used and the observations reported here, tip inducing motion is unlikely. The Cu rows are quasiperiodically spaced independent of the STM scan direction. As

![Image](035420-4)

**FIG. 4.** (a) LEED pattern of the periodic structure obtained at 39 eV. (b) 250 Å × 250 Å STM image. The arrows show five directions of the periodic structure. (c) 70 Å × 70 Å region of the periodic structure. (d) Segment of the LEED pattern shown on Fig. 4(a) (inverted intensity for clarity). (e) Fast Fourier transform calculation from the periodic model described in the text.

reported previously, there is a correlation of the row sequencing across steps.

**C. Structure after annealing**

After deposition of 25 ML of Cu on the Al-Pd-Mn surface, the LEED pattern disappears. We observed that upon annealing the sample to 570 K for 10 minutes, a LEED pattern is obtained [see Fig. 4(a)]. A large amount of Cu desorbs into the bulk, leaving an equivalent coverage of 1.5±0.5 ML of Cu as measured by AES. STM measurements reveal a structure. The film can be understood as five periodic domains rotated from each other by 72°. These five orientations are indicated by the five arrows on Fig. 4(b). This structure is not quasiperiodic but the five orientations of the domains are parallel to the five main axes of the quasicrystalline substrate. Higher magnification images [see Fig. 4(c)] allow us to determine the lattice parameters X and Y within the domains. They are equal to 4.2±0.2 Å and 8.4±0.3 Å, respectively, and therefore Y=2X within the accuracy of our measurements. In order to understand the LEED pattern obtained, a model is proposed and consists of several domains of atomic rows with Y=2X rotated in five directions as seen on Fig. 4(c). A fast Fourier transform calculated from this model is shown on Fig. 4(e). Figure 4(d) is a segment of the LEED pattern of Fig. 4(a) (inverted contrast for clarity). Comparing Figs. 4(d) and 4(e), the resemblance is clear. All Bragg reflections recorded on Fig. 4(d) are present in the calculated FFT. Thus, the model considered here provides a simple explanation of the LEED pattern observed. The lattice parameters measured do not match those of a pure Cu structure. It is highly probable that Cu alloys with the substrate and an alloy could result from this phase transformation.

**IV. DISCUSSION**

**A. Growth mode of the Cu film**

When dealing with metal-on-metal adsorption, one can predict the growth morphology, assuming the system is in
ery. Fourné et al. have used the above equation to understand the growth of Ag on the Al-Pd-Mn surface. The value of \( \gamma_{Ag} \) \((1.72 \text{ J/m}^2)\) is comparable to \( \gamma_{Al} \) \((1.199 \text{ J/m}^2)\), Al being the major constituent of the quasicrystal top-most surface layers.\(^5\) Upon Ag deposition, islands initially grow vertically. The roughness of the film could be explained by a high interfacial energy.\(^17\) Here, \( \gamma_{Cu} \) \((1.952 \text{ J/m}^2)\) is much higher than \( \gamma_{Al} \) and following Ref. 23 one should expect an initial 3D growth. Instead Cu wets the substrate and a layer-by-layer growth is observed up to 8 ML. Below 1 ML, irregular shaped islands of monatomic Cu height are obtained with no indication of periodic domains are present through extracted from LEED measurements at low temperature, led to the formation of a film with a close-packed (111) structure modulated by a quasiperiodic superstructure.\(^29\) The one-dimensional height modulation of the structure yields quasi-periodically ordered rows as observed by STM.\(^{29,30}\) There are similarities between the two systems in that Fibonacci sequences and the golden ratio are identified in both.\(^20,30\) The difference between the two structures is that one is grown on a periodic substrate and one is grown on a quasicrystal substrate; thus the Ag film develops a quasicrystalline structure in response to the periodic potential of the GaAs, and while the Cu forms a structure in response to the aperiodic potential of the quasicrystal, and is therefore “pseudomorphic.” The Ag film can be considered to be a weakly modulated (in 1D) Ag(111) structure, whereas the Cu film is really a (higher-order) commensurate structure (in 1D).

\[ \gamma_f + \gamma_i - \gamma_s \leq 0, \] 

where \( \gamma_f \), \( \gamma_i \), and \( \gamma_s \) are the surface free energies of the adsorbate and the substrate, respectively, and \( \gamma_s \) is the interfacial energy. Fourné et al. have used the above equation to understand the growth of Ag on the Al-Pd-Mn surface. The value of \( \gamma_{Ag} \) \((1.72 \text{ J/m}^2)\) is comparable to \( \gamma_{Al} \) \((1.199 \text{ J/m}^2)\), Al being the major constituent of the quasicrystal top-most surface layers.\(^5\) Upon Ag deposition, islands initially grow vertically. The roughness of the film could be explained by a high interfacial energy.\(^17\) Here, \( \gamma_{Cu} \) \((1.952 \text{ J/m}^2)\) is much higher than \( \gamma_{Al} \) and following Ref. 23 one should expect an initial 3D growth. Instead Cu wets the substrate and a layer-by-layer growth is observed up to 8 ML. Below 1 ML, irregular shaped islands of monatomic Cu height are obtained with no indication of second-layer island nucleation [similar to Cu/Pd(100) (Ref. 25)]. This discrepancy could have two origins. First, the above equation is not applicable because the thermodynamic equilibrium is not reached. Second, at submonolayer coverage, alloying or intermixing is taking place. The latter would imply that intermixing occurs at the Cu/Al interface, alloying or intermixing is taking place. The latter would imply that intermixing occurs at the Cu/Al interface, alloying or intermixing is taking place. The latter would imply that intermixing occurs at the Cu/Al interface, alloying or intermixing is taking place.

C. Stability of the film at room temperature

At coverages above 8 ML, changes in surface morphology after the deposition has stopped can be observed in Fig. 3. These changes indicate that the film is not in equilibrium at room temperature at these coverages. There is a net diffusion of Cu atoms from lower terraces to higher terraces, leading to a structure having a rougher height profile. Recently Zhu et al. have used first-principles total-energy calculations to demonstrate that under certain conditions in the growth process, adatoms may easily climb monatomic-layer-height steps on fcc(110) surfaces via a place exchange mechanism, leading to the formation of facets on surfaces that are initially flat.\(^27\) A similar mechanism might account for the increasing roughness of the film with coverage. If the kinetics of this mechanism are slow compared to the deposition rate, initially flat terraces may be formed which evolve more slowly into facets or otherwise rough features.

The quasiperiodic Cu structure transforms to a periodic alloy structure after annealing the system. The transformation to this alloy structure involves massive mass transport and mass substitution which is apparently facilitated at the higher temperature.

V. CONCLUSIONS

Along the Cu rows in the aperiodic thin film, the atoms are arranged in a periodic manner with an interatomic spacing extracted from LEED measurements at low temperature and equal to 2.5±0.1 Å. This spacing was not observed by STM even after cooling the Cu film to 25 K. A delocalized electron density could explain the lack of resolution along those rows. Spontaneous mass transport has been observed using STM and reveals that ascending adatoms are responsible for island formation above 8 ML. Periodic domains are
obtained after annealing the Cu thin film to 570 K. Within each domain, the lattice parameters are measured at 4.2±0.2 Å and 8.4±0.3 Å. Future experiments will probe the electronic properties of the film, in particular whether or not a pseudogap at the Fermi level is preserved within this system. This could have a significant impact on the physical and chemical properties of this film.

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