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# $C_{60}$ adsorption on an aperiodically modulated Cu surface

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**Abstract.** Copper deposited on the five-fold surface of icosahedral Al-Pd-Mn forms domains of a structure whose surface has a one-dimensional aperiodic modulation. It is shown that  $C_{60}$  deposited on this aperiodic film has highly reduced mobility as compared to  $C_{60}$  deposited on periodic Cu surfaces. This finding is explained in terms of the recently proposed structural model of this system.

## 1. Introduction

The interaction of adsorbing species with solid surfaces is of fundamental importance in epitaxial growth and nanostructure formation. The competition between adsorbate-adsorbate and adsorbate-substrate interactions leads to a wide spectrum of behaviour. When lattice misfit is minimal, epitaxial growth may occur; where misfit is appreciable the resulting interfacial strain may be accommodated pseudomorphically, by misfit dislocations, or by rotational epitaxy along high-symmetry directions of the substrate. Such effects have been extensively studied in simple model systems such as rare gas adsorbates on graphite [1] and alkali atoms on metal surfaces [2].

Since its discovery [3],  $C_{60}$  has also been employed as a model system in the study of ordering of two-dimensional molecular solids on surfaces. The interaction potential in solid  $C_{60}$  is composed of a long-range attractive van der Waals component and a repulsive short-range component, the counterbalance of which stabilises the molecular solid. On a surface, these interactions also compete with the adsorbate-substrate interactions and a wide range of behaviour is found, as the strength of this adsorbate-substrate interaction varies with the chemistry and geometry of the surface. On single crystal metal surfaces, behaviour ranges from epitaxial growth [4] to rotational epitaxy [5], to interfacial reconstruction with adlayer buckling and rotation [6]. On (111) semiconductor surfaces, epitaxial growth is also observed [7], while on anisotropic surfaces such as Si(100)(2×1) the  $C_{60}$  overlayer has been found to be uniaxially incommensurate along the the dimer row directions [8].

It is of great interest to extend such studies to the case of the interaction of  $C_{60}$  with surfaces which have non-periodic, through well-ordered geometries. On such surfaces, the possibility of the accommodation of lattice misfit through rotational epitaxy is removed, and hence the formation of incommensurate structures is unavoidable. The surfaces of quasicrystals fall into this category. Quasicrystals are metallic alloys whose surface structure can be thought of as a physical realization of a Penrose tiling, which is a two-dimensional quasiperiodic pattern [9].

With the constraint of periodicity removed, such materials often display five-fold and ten-fold rotational symmetries which are not observed in periodic solids. The surfaces of quasicrystals have been found to be essentially terminations of the bulk structure, without reconstruction and minimal relaxation [10–14].

Unfortunately,  $C_{60}$  does not form ordered overlayers on quasicrystal surfaces. On the five-fold surface of AlPdMn [15, 16] and the ten-fold surface of AlNiCo [17], strong chemical interaction with the substrate binds the molecules strongly, inhibiting diffusion and leading to the formation of disordered overlayers. However, studies are emerging in which  $C_{60}$  is not deposited directly on to the clean quasicrystalline surface, but instead upon a quasicrystalline interfacial layer such as Pb/Al-Ni-Co, one purpose of which is to tune the reactivity of the quasicrystalline system [18].

It has previously been found that Cu, Ni, Fe and Co, when deposited on the five- and ten-fold surfaces of Al-based quasicrystals, tend to adopt the rotational epitaxial growth mode [19–27], in which crystalline islands grow in various azimuthal orientations matching the rotational symmetry of the underlying quasicrystal. For Cu and Co, further interesting behaviour is observed in a modulation of the islands to exhibit some aperiodic ordering at their surfaces. The Cu/AlPdMn system has been well-studied using scanning tunneling microscopy (STM) [19], low-energy electron diffraction (LEED) [20], medium-energy ion-scattering spectroscopy (MEIS) [21] and dynamical LEED (LEED-IV) [22, 28]. Upon adsorption on the five-fold surface of icosahedral Al-Pd-Mn, no ordering is observable in a Cu film up to 3 ML by STM or LEED. As coverage increases beyond this value, pentagonal angles in domain edges become apparent, as does a row structure (manifested as a  $z$ -modulation) on the surface of the film. The rows are spaced according to a one-dimensional Fibonacci sequence with separations  $S = 4.6 \text{ \AA}$  and  $L = 7.4 \text{ \AA}$  as measured by STM. The LEED pattern reappears concurrently with observable ordering in STM images, and is composed of a pattern based on a periodic Cu-Cu separation along rows and a continuous streaking due to diffraction from the 1D Fibonacci sequence, in 5 azimuthal orientations arising from the alignment with high-symmetry axes on the quasicrystal surface.

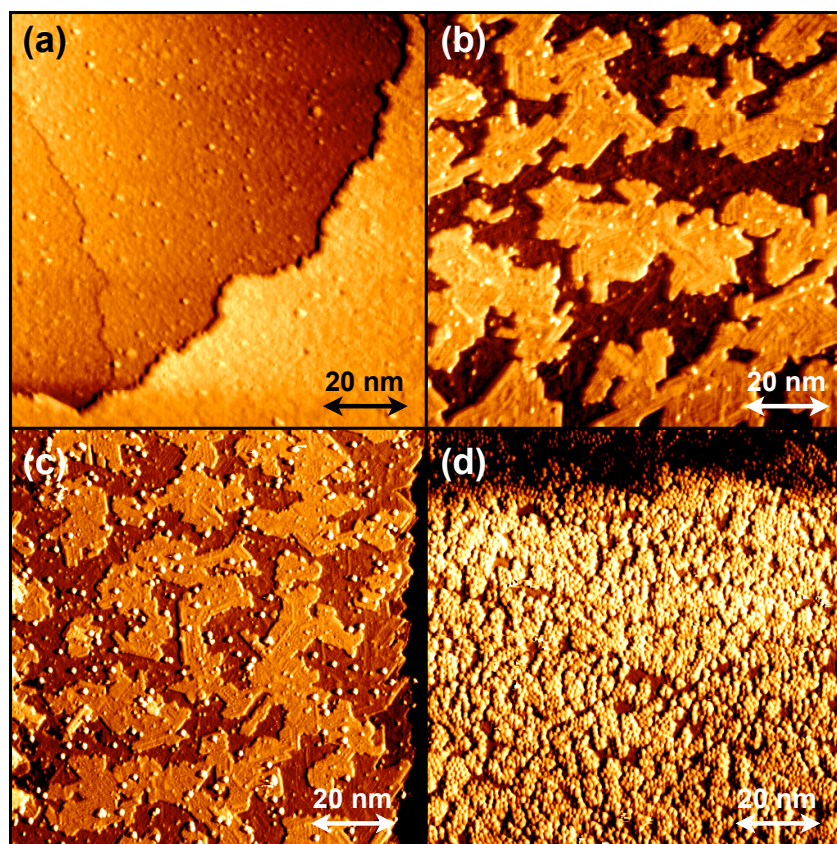
Smerdon *et al.* proposed a structure for the thin film based on MEIS results that identified the crystalline phase making up the rows as fcc Cu with the (100) face parallel to the surface [21]. This picture of the film does not explain why the row structure is observable by STM, nor why there is no ordering below 3 ML coverage. However, analysis of recent LEED-IV results [28] suggests that the phase is in fact body-centred tetragonal (bct) Cu that grows at an angle to the surface normal. This model provides an explanation of both observations mentioned above.

In this work, we explore the differences between  $C_{60}$  adsorption on single crystal ideal Cu surfaces from existing studies and  $C_{60}$  adsorption on the quasiperiodically arranged form of Cu.

## 2. Experimental conditions

The adsorption studies were carried out in an Omicron variable temperature STM (VT-STM) UHV chamber. The base pressure of the system was  $1 \times 10^{-10}$  mbar. The Al<sub>70</sub>Pd<sub>21</sub>Mn<sub>9</sub> quasicrystal sample, produced at Ames laboratory using the Bridgman method, was polished successively with 6  $\mu\text{m}$ , 1  $\mu\text{m}$  and 1/4  $\mu\text{m}$  diamond paste before introduction to vacuum and thereafter was prepared in cycles consisting of 45 minutes sputtering with 3 keV Ar<sup>+</sup> ions followed by at least 4 hours annealing to 950 K, using electron-beam heating, up to a total annealing time of 20 hours.

All evaporation of adsorbates was carried out with the sample at or close to room temperature. The Cu evaporation was performed using a simple filament source consisting of a W wire wrapped around a piece of OFHC Cu. The  $C_{60}$  evaporation was performed using a thin W filament wrapped around a Pyrex crucible containing  $C_{60}$ , with temperature regulated using a K-type thermocouple tightly strapped to the crucible. During evaporation the W filament glowed yellow and was approximately 3 cm away from the sample. Evaporating temperatures in the range 500 K - 520 K were used and the chamber pressure did not exceed  $4 \times 10^{-10}$  mbar during evaporation.



**Figure 1.** (a); A  $100\text{ nm}\times 100\text{ nm}$  image of a clean Al-Pd-Mn surface, (b); A  $100\text{ nm}\times 100\text{ nm}$  image of the  $4.5 \pm 0.1\text{ ML}$  Cu layer deposited on the Al-Pd-Mn surface. The lighter rows have previously been identified as strain-related defects [19], the white spots are contamination, (c);  $0.025\text{ ML}$   $\text{C}_{60}$  adsorbed atop the Cu layer, showing an absence of island formation, (d);  $0.8\text{ ML}$   $\text{C}_{60}$  adsorbed atop the Cu layer, showing some evidence of orientation of rows of  $\text{C}_{60}$ .

The sample was maintained at room temperature throughout the experiment.

### 3. Results and discussion

Fig. 1 shows the starting surface. Following the deposition of  $4.5 \pm 0.1\text{ ML}$  Cu, the previously reported [19] one-dimensionally aperiodic structure is observed via STM as shown in figure 1(b). The Cu film on this substrate is highly complex, and has only recently been adequately described [28]. The film structure is suggested to be a collection of orthorhombic domains oriented off-normal to the substrate such that the  $\text{bcf}(100)$  terraces are cut according to the substrate Fibonacci sequence, producing a similar one-dimensional sequence on the film surface parallel to the substrate/film interface. This suggests that there are potentially a considerable amount of inequivalent adsorption sites of high coordination at the surface of this film.

Following formation of the Cu film,  $\text{C}_{60}$  molecules were deposited, up to a maximum coverage of  $0.8 \pm 0.1\text{ ML}$  coverage. At lower coverages of  $0.02 \pm 0.005\text{ ML}$  (as shown in figure 1(c)),  $\text{C}_{60}$  molecules are observed to be of a constant height above the substrate of  $0.6 \pm 0.1\text{ \AA}$ , independent of tunneling conditions.  $\text{C}_{60}$  molecules do not coalesce to form islands, leading us to conclude that the molecules are not mobile at room temperature on this surface.

Most molecules also exhibit intra-molecular features in STM, indicating that the molecules

are not rotating freely on the film. This is observed in general with  $C_{60}$  adsorption on transition metal substrates [6,29–31]; however, there is then some consistency in the rotational alignment of the molecules corresponding to a particular adsorption site. We do not observe such consistency.

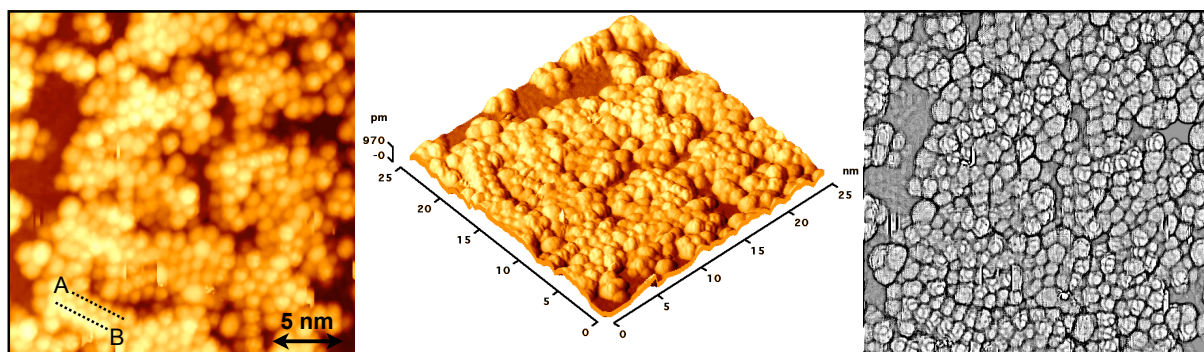
At higher coverages of between 0.5-0.8 ML, some  $C_{60}$  row structure becomes apparent in some parts of the film, as shown in figure 1(d). Adjacent rows are found to have a difference in height; the average  $z$ -difference as shown in fig. 2 is 1.3 Å, indicating that these higher rows cannot be a second layer of  $C_{60}$ .

These observations contrast with those for adsorption on periodic Cu substrates. The absence of  $C_{60}$  island formation at room temperature and low coverage is unusual contrary to that observed for  $C_{60}$  on single-crystal Cu(100), (110) and (111) surfaces [29, 31, 32]. In all these cases, although the molecules are tightly-bound enough to the substrate to adopt a particular orientation (or set of orientations) visible in terms of cage structure, the molecules may still diffuse to decorate step edges and form islands at sub-monolayer coverage.

This indicates that in the present system, diffusion of  $C_{60}$  molecules is inhibited. As the Cu film is much rougher than a single crystal surface, it might be expected that roughness is the inhibiting factor. Were the roughness parallel to the Cu rows comparable to the roughness of a flat terraced Cu surface, although diffusion *across* the rows would be inhibited,  $C_{60}$  molecules might be expected to diffuse more or less freely *along* them. In this case it is likely that the domain steps would be decorated first, similarly to the single-crystal Cu systems. This is not the case; with a thresholded Sobel edge-finding algorithm,  $(26 \pm 5)\%$  of the surface is found to be within one  $C_{60}$  diameter of a step edge, and the population of  $C_{60}$  molecules located within one  $C_{60}$  diameter of a step edge is found to be  $(30 \pm 10)\%$ , so, within the measurement error, there are the same number of  $C_{60}$  molecules near step edges as there would be through random adsorption. In fact, the  $z$ -range measured using STM along the rows on tilt-corrected data is on average 30 pm, three times more than that measured in a similar fashion over an area of fcc(110) Cu. We assume that this inherent roughness must therefore be a sufficient barrier to diffusion such that, following impingement, molecules remain at the closest local potential energy minimum. This is a unique result for a transition metal surface, that may be explained by the model of the Cu film proposed by Pussi *et al.* [28]. As explained above, this model comprises domains of bct Cu oriented in five directions consistent with the substrate high-symmetry axes. The domains are offset parallel to the substrate surface, resulting in a cut plane that gives the Fibonacci sequence in the pattern of steps at the film surface. This means that the entire film surface is a pattern of step edges. It is expected that  $C_{60}$  molecules would be immobile once located at a step edge.

$C_{60}$  molecules chemisorbed on transition metal substrates generally exhibit either a three-lobed feature or a ring feature parallel to the crystallographic plane of the surface [6, 29, 31]. The three-lobed feature indicates that the molecule is chemisorbed with hexagonal faces parallel to the surface, the ring feature indicates that pentagonal faces are parallel to the surface. This shows that, on these substrates, an axis of high symmetry (either three-fold or five-fold in the examples given, but two-fold axes are also possible) is oriented perpendicular to the surface crystallographic plane, resulting in rotational symmetry of individual molecules around the normal to the surface crystallographic plane. Such rotational symmetry of individual molecules is very rarely observed in this study, as can be seen in the Laplace filtered image on the right side of fig. 2. This evidence also supports the model that the Cu film structure is vicinal, with a primary crystallographic axis at an angle to the quasicrystal five-fold plane [28]s.

The row formations exhibited by  $C_{60}$  at higher coverage are reminiscent of those observed for adsorption on the Cu(100) and Ni(110) surfaces [31, 32]. Upon adsorption on Cu(100) and Ni(110) surfaces at room temperature,  $C_{60}$  causes reconstruction of the substrate surface, identifiable by the differing heights of  $C_{60}$  molecules above the surface observed. For example, a single row of  $C_{60}$  molecules may sit higher than a row either side. If the height difference



**Figure 2.** Left: A 25 nm×25 nm image of 0.8 ML  $C_{60}$  adsorbed atop a  $4.5 \pm 0.1$  ML Cu film on the five-fold Al-Pd-Mn surface (fast-scan direction is vertical). The  $z$ -separation of profiles along A and B is on average 1.3 Å; Centre: The image rendered in 3 dimensions, showing the flatness of the film; Right: A Laplace filtered version of the image, showing intra-molecular features.

is incompatible with a  $C_{60}$  interplanar step height, then it must be ascribed to the underlying surface. In the case of  $C_{60}/Cu(100)$  [31], for each height of  $C_{60}$  within a  $C_{60}$  island, i.e., for each unique type of adsorption site in terms of substrate reconstruction, the  $C_{60}$  molecule adopts a particular orientation with respect to the substrate. To a degree, we observe such phenomena in the present system; for example, the row of molecules denoted B in fig. 2 sits 1.3 Å higher than its neighbours. The step height of a second layer of  $C_{60}$  is 8.2 Å [33] and the step height of the Cu film is  $1.9 \pm 0.1$  Å [19]. The interlayer spacing of the bct structure is 0.68 Å [28], meaning that atomic rows could be removed from the Cu layer giving positions of  $C_{60}$  with a  $z$ -quantization of 0.68 Å. Hence a reconstruction is a plausible explanation for such observations, especially in the context of other studies of  $C_{60}$  on transition metals.

#### 4. Conclusions

$C_{60}$  molecules on a Cu film on the five-fold surface of icosahedral Al-Pd-Mn.  $C_{60}$  molecules show markedly different adsorption behaviour as compared to deposition on low-index single crystal Cu surfaces. The molecules have extremely limited mobility at room temperature and do not form islands or decorate step edges, instead remaining where they impinge on the surface. At higher coverages (above 0.5 ML  $C_{60}$ ), there is some suggestion of reconstruction of the underlying Cu film in the observed differing heights of adjacent rows of consistently orientationally aligned  $C_{60}$  molecules. The features of adsorption of the  $C_{60}$  molecules can be interpreted in terms of the recent model proposed by Pussi *et al.* [28].

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