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Abstract
We present a review of experimental studies of adsorption systems where pseudomorphic growth on quasicrystal surfaces has been observed. From these studies, we correlate information on the known or suggested adsorption and nucleation sites. For fivefold surfaces of icosahedral quasicrystals, two favoured locations emerge: the centres of equatorially truncated pseudo-Mackay clusters, and the centres of pentagonal hollows. The information on adsorption sites on decagonal quasicrystals is less definitive. Nevertheless the correlation of known information leads to a simple picture of pseudomorphic growth, at least for the first monolayer. We also remark on the possibilities for studies using quantitative surface structural techniques.

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

1. Introduction

Quasicrystals are aperiodic materials which possess long-range order but without translational symmetry [1]. They are usually trimetallic and are formed within a narrow stoichiometrical range. Since it was established that their surfaces could be prepared in vacuum such that they exhibit a step/terrace structure, there has been interest in using these surfaces as substrates for epitaxy. This is motivated partly by the aspiration of forming single-element quasiperiodic monolayers and ultimately films. Such systems would facilitate the study of aperiodic order and its consequences on physical properties but with reduced chemical complexity. It is also of great interest to study such systems and compare the epitaxial behaviour with that observed on periodic substrates. In this respect there have been several surprising findings [2, 3] which have extended our understanding of epitaxy in general.

There are essentially three possibilities for epitaxial growth on quasicrystal substrates [4]. The first is the formation of a crystalline film which has no structural relationship to the substrate. The second is the formation of a crystalline film which is orientationally aligned with the substrate (rotational epitaxy). The third possibility is that of pseudomorphic growth where the film grows in a commensurate structure (necessarily

different from its normal elemental crystalline form) in a manner dictated by its interaction with the substrate [5]. This latter growth mode is required for the achievement of a single-element quasiperiodic structure.

To date, pseudomorphic growth has been observed in a relatively small number of systems [6, 7]. Although quasiperiodic modulations have been found which persist through several crystalline atomic overlayers [2, 8], pseudomorphic ordering has only been observed in coverages up to a monolayer. Furthermore, in only a subset of these studies has any structural information been deduced about the initial nucleation and subsequent growth and structure of the system.

This information has usually been obtained using scanning tunnelling microscopy (STM). Although the pitfalls in using STM as a structural tool are well documented (see e.g. [9, 10]), in favourable cases adsorption site determination has been achieved and is in agreement with studies using other methodologies. This is particularly so when density functional theory (DFT) calculations are used in conjunction with STM to provide simulated images [11]. Indeed in all cases where adsorption/nucleation sites have been identified to date, STM has been used in the process.

The scope of this review is as follows. The paper will focus only on experimental studies of pseudomorphic systems where structural information on the adsorption or nucleation site and/or on the structure of the overlayer has been deduced.

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This precludes studies using diffraction techniques alone, and also systems where evidence of pseudomorphic behaviour at sub-monolayer to monolayer coverages is speculative or absent (e.g. i-Al–Pd–Mn/Cu [2, 12]). Systems where rotational epitaxy without pseudomorphism is observed are discussed in other articles in this issue. In general, we will not comment in detail on modelling studies, except where they are relevant to one of the experimental systems being discussed. The aims of the paper are to establish whether any trends have emerged among the small number of systems studied to date, and to clarify the criteria for growth of pseudomorphic monolayers. We also speculate on the possibilities of applying more quantitative surface structural techniques to any of these systems to provide quantitative confirmation of results deduced using STM.

The paper is organized as follows: in section 2 we review the known structural facts in systems where pseudomorphic behaviour has been observed on icosahedral and decagonal quasicrystal substrates. The studies are presented in groups according to the substrate used and within these groups according to chronological order of the appearance of the information on adsorption and growth. In section 3 we identify the common trends which emerge from this review and speculate on the possibilities of studying these systems with more quantitative structural techniques. Section 4 gives a summary of our findings.

2. Review of adsorption systems

2.1. C_{60} adsorption on the 5-f Al–Pd–Mn surface

With the aim of forming a quasiperiodic overlayer on the fivefold Al–Pd–Mn surface, Buckminsterfullerene molecules (C_{60}) were selected as adsorbates. This choice was based on the molecular geometry which displays hexagonal and more importantly pentagonal facets likely to match the substrate symmetry. In addition, the C_{60} cage diameter (7.1 Å) is comparable to specific atomic motifs such as the width of fivefold pentagonal hollows (also known as 'dark stars', 7.4 Å) present on all terraces of the quasicrystal substrate. Previous studies had shown that the quasiperiodic surface structure is immediately lost upon molecular adsorption [13–15]. This disordering is thought to arise from the formation of strong chemical bonds and dissociation of the adsorbed molecules when reaching the sample. C_{60} molecules tend to stay intact upon adsorption and form fairly weak bonds to the substrate.

At low coverage, the C_{60} molecules were observed to form a dispersed layer without any clustering or step-edge adsorption. The formation of an hexagonal overlayer is often observed e.g. for C_{60} adsorption on an Al(111) surface [16]. In this case, as the dose increased, no evidence was found for such ordering. The density of the molecules increased proportionally to the dose time, as evidenced by Auger electron spectroscopy (AES) and STM measurements. The LEED pattern started to degrade and finally vanished with the completion of the first monolayer. Fast Fourier transforms (FFTs) and autocorrelation function calculations carried out on several STM images up to 1 ML indicate a lack of long-range ordering of the molecules. Thus it was postulated that
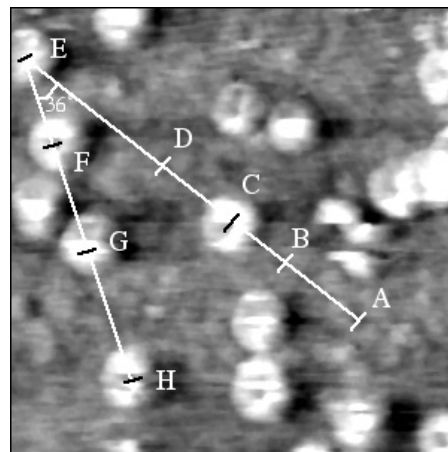

Figure 1. STM image (150 Å × 150 Å) for a coverage of 0.065 ML of C_{60} molecules. The adsorption of the molecules on top of fivefold hollow sites leads to a τ-scaling relationship in the inter-molecular distances. After [18].

the LEED pattern recorded in the sub-monolayer regime was due to the residual part of the substrate not populated with C_{60} molecules.

At 0.065 ML, the apparent heights of the adsorbates measured by STM can be organized into three distinct classes. These height differences are indicative of either a topographical contribution due to bonding in pentagonal hollow sites of various depths or of a reduction in the local density of states due to bonding to different atomic species leading to a stronger interaction with the substrate [17]. A combination of both effects is likely to take place on such a complex surface. In addition, annealing the C_{60} monolayer to 600 K caused partial desorption of the adsorbates leaving an estimated coverage of 0.25 ML at the surface. This observation lends support to the scenario of adsorbates occupying a range of bonding sites at the quasicrystal surface.

We now consider possible local ordering of C_{60} molecules at the quasicrystal surface at low coverage. Figure 1 shows a high resolution STM image of 0.065 ML of C_{60} molecules. Despite a reduced resolution of the substrate due to the molecule height, three unoccupied pentagonal hollow sites can be marked with white dashes and are labelled as A, B, and D. The black dashes indicating the centre of the adsorbates are labelled C, E, F, G and H. Within the accuracy of the measurements, the following distance relationships exist between the C_{60} molecules and pentagonal hollows:

$$[AE] = \tau[AD] = \tau^2[AC] = \tau^3[AB] \qquad (1)$$

and similarly

$$[EH] = \tau[EG] = \tau^3[EF]. \qquad (2)$$

As shown by Schaub *et al* [19], pentagonal hollows are aligned along a Fibonacci pentagrid. Hence the distances separating the depressions are subject to a τ-scaling relationship. This means that if the distance between two pentagonal hollows is multiplied by the golden ratio τ or multiples of τ, the resulting distance should locate another such hollow on the same line [20]. These observations lead
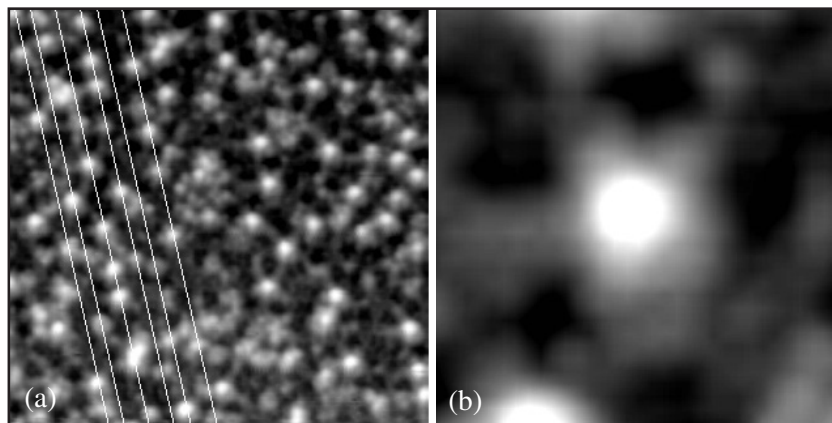
Figure 2. (a) STM image (200 Å × 200 Å) for a coverage of 0.25 ML of Si on the fivefold surface of i-Al–Pd–Mn. A 1-d Fibonacci sequence has been extracted from the visible Al–Pd–Mn substrate following the method described by Schaub *et al* [19]. The Si adatoms predominantly lie along these lines. (b) 33 Å × 33 Å image showing a Si atom adsorbed on top of an equatorially truncated pseudo-Mackay cluster or 'white flower'. After [21].

us to tentatively assign the position of the adsorbates on top of the pentagonal hollows.

To conclude, it appears that C_{60} molecules adsorb randomly on the surface with a range of bonding sites. Although a 2-d quasiperiodic overlayer could not be formed using C_{60} molecules, local τ-scaling relationships were identified between adsorbates with bonding of these molecules in pentagonal hollows.

2.2. Si adsorption on the 5-f Al–Pd–Mn surface

The interaction between semiconducting adsorbates and quasicrystals surfaces is an intriguing prospect. The formation of a Si monolayer on a quasicrystalline substrate would allow the study of the interplay between a quasicrystalline pseudogap and a semiconducting band gap.

Figure 2(a) shows individual Si atoms adsorbed on the fivefold Al–Pd–Mn surface for a coverage of 0.25 ML. The relative height of the adsorbates (appearing as bright protrusions) was found to be monoatomic and measured at 2.13 ± 0.10 Å. The resolution of the quasicrystal substrate was sufficient to distinguish the underlying surface motifs, in particular the pentagonal hollows and the ring-like features also known as white flowers [12, 22], which were interpreted as equatorially truncated pseudo-Mackay ('M') clusters surrounded by five 'hanging' Bergman ('B') clusters. These two entities, composed of 51 and 33 atoms respectively, can be interpreted as the basic building blocks for the icosahedral quasicrystal structure. By connecting the edges of the pentagonal hollows [19], a 1-d Fibonacci sequence with $L = 7.35 \pm 0.20$ Å and $S = 11.90 \pm 0.20$ Å was identified on the quasicrystal surface. The remarkable degree of alignment of the adatoms with the *SLLSL* sequence drawn on figure 2(a) indicates a quasiperiodic ordering of the Si adsorbates across the i-Al–Pd–Mn surface. An identical Fibonacci-like alignment could be measured in the remaining four directions.

To further confirm the quasiperiodic ordering of the adatoms, FFT and autocorrelation functions were calculated

from STM images. Only Si atoms were selected for these calculations through a thresholding of the image. The FFT displays three main rings of ten spots with radii related to each other by powers of the golden ratio τ. The positions of the low energy electron (LEED) spots were commensurate with those obtained from STM images of the clean i-Al–Pd–Mn surface. The two-dimensional autocorrelation function calculated indicated a spatial correlation of the Si atoms over distances of at least 130 Å. A careful analysis of the local environment around Si adatoms suggests a unique nucleation site at this low coverage. A preferential adsorption on a quasiperiodically distributed site could indeed explain this aperiodic array of Si atoms. The resolution of the quasicrystal substrate around Si atoms (see figure 2(b)) allows the identification of the nucleation site as the centre of the white flower. Hence Si atoms sit on top of truncated pseudo-Mackay clusters.

Simulations were performed for Si adatoms adsorbed on top of the white flower and on top of alternative sites. The comparison between radial distribution functions calculated from theoretical and experimental autocorrelation functions point towards the white flower as adsorption site for Si atoms. This result is also supported by the distances measured between adsorbate-to-adsorbate, adsorbate-to-white-flower or pentagonal hollow patterns. Recent *ab initio* calculations performed on the clean fivefold i-Al–Pd–Mn surface have revealed valence charge maxima around the Mn atom decorating the centres of the truncated pseudo-Mackay clusters [23]. These charge density maxima were postulated to be the reason for Si adsorption at these locations. This could be related to the tendency of the Si to form directional bonds via sp^3 hybridization of its atomic orbitals rather than via the optimization of the local coordination.

Finally, the maximum number of truncated pseudo-Mackay clusters available on the surface plane has been estimated from the Katz–Gratias–Boudard model at 0.2 nm^{-2} [24]. Once all sites are populated (coverage > 0.25 ML), Si clusters start to form and coexist with individual atoms at the surface. As the coverage is increased, the LEED pattern slowly
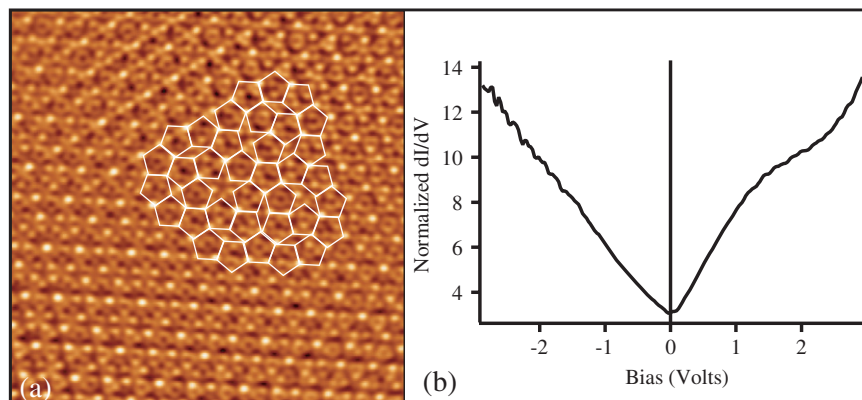
Figure 3. (a) High resolution STM image (250 Å × 250 Å) of 1 ML of Pb; the raw data has been Fourier-filtered to emphasize the ordered part of the structure. (b) Scanning tunnelling spectroscopy measurements performed on 1 ML of Pb annealed on the quasicrystal surface. After [21].

degrades and finally disappears upon completion of the first monolayer. Above 1 ML, three-dimensional growth is observed. The monotonic increase in the Si–Al peak-to-peak ratio as measured by AES rules out any Al–Si alloy formation.

Thus a quasiperiodic array of Si adatoms is obtained at low coverage, due to the decoration of a unique nucleation site quasiperiodically distributed on the surface and identified as the equatorially truncated pseudo-Mackay cluster.

2.3. Pb adsorption on the 5-f Al–Pd–Mn surface

In this study, Pb was deposited on the fivefold i-Al–Pd–Mn surface. The choice of this adsorbate was partly dictated by the reported quantum size effects (QSE) measured upon adsorption on the Cu(111) and Si(111) surfaces [25, 26]. The presence of a pseudogap at the quasicrystalline surface could also influence the growth mode of Pb adatoms and the electronic properties of Pb thin films.

Lead adsorption was first monitored using AES and x-ray photoelectron spectroscopy (XPS). From these measurements, the rate of adsorption was found to decrease with increasing Pb coverage. The reduction of the sticking coefficient upon deposition was further confirmed by STM dosing the same region while scanning. With one monolayer adsorbed, the growth of a second layer was not observed within the range of fluxes (2.5×10^{-3}–2.5×10^{-2} ML s^{-1}) and substrate temperatures (57–653 K) used. Total desorption of the Pb monolayer was found to occur upon annealing the sample to 670 K. For comparison purposes, Pb adsorption was carried out in parallel on an Al(111) surface. The shape and position of Pb 4f core levels recording on the quasicrystal surface (Pb coverage of 1 ML) and on Al(111) surface (Pb coverage of 1 ML) were identical. The Al 2p core levels recorded on the clean quasicrystal surface prior to and after deposition of 1 ML of Pb were unchanged. These observations are consistent with the immiscibility of Al and Pb. The density of the Pb monolayer (0.09 atom Å^{-2}) adsorbed on the quasicrystal was also deduced from these XPS measurements.

Self-assembled Pb pentagonal islands were observed at sub-monolayer coverage. These fivefold clusters were found to be monoatomic in height with an edge length measured at 4.9 ± 0.3 Å, i.e τ bigger than the smallest Al pentagons present on the clean fivefold surface [22]. This τ-inflation of the basic structural unit causes a τ-scaling of the complete monolayer structure. The pentagons present the same orientation across the sample and form regardless of the deposition rate used. This fact suggests an heterogeneous nucleation process at a specific trap site [27–29]. The increasing number of pentagonal islands with Pb coverage leads to the formation of an interconnected network. The completion of the overlayer is obtained by Pb adatoms filling the network interstices. As demonstrated by the LEED patterns recorded, the Pb thin film is quasiperiodic in nature. Its structural quality can be improved either by subsequent annealing of the film to 653 K or by Pb deposition with the substrate maintained at 653 K. Figure 3(a) shows an STM image obtained following the latter procedure. A Penrose P1 tiling [30], using τ-inflated tiles compared to those described in previous work [22], is superimposed on the STM image and emphasizes the quasiperiodic ordering of Pb.

Regarding the electronic structure of the film, figure 3(b) shows scanning tunnelling spectroscopy (STS) measurements revealing the presence of a pseudogap on the Pb monolayer. The pseudogap is larger on the Pb structure than on the clean fivefold surface. In a nearly free-electron-like system, the width of the gap scales with the lattice potential $|V_K|$, the latest being the product of the geometrical structure factor and of the form factor. The form factor is related to the atomic number of the element, hence the opening of a larger gap is expected on the quasiperiodic lead film. From this adsorption study, it appears that the quasiperiodic structure of the film is responsible for the formation of the pseudogap [21].

2.4. Bi adsorption on the 5-f Al–Pd–Mn surface

The first study to find evidence for quasicrystalline single-element monolayers was conducted by Franke *et al* [31]. They investigated the growth of Bi and Sb on the fivefold surface of i-Al–Pd–Mn and the tenfold surface of d-Al–Ni–Co by He atom scattering (HAS) and LEED [31]. This
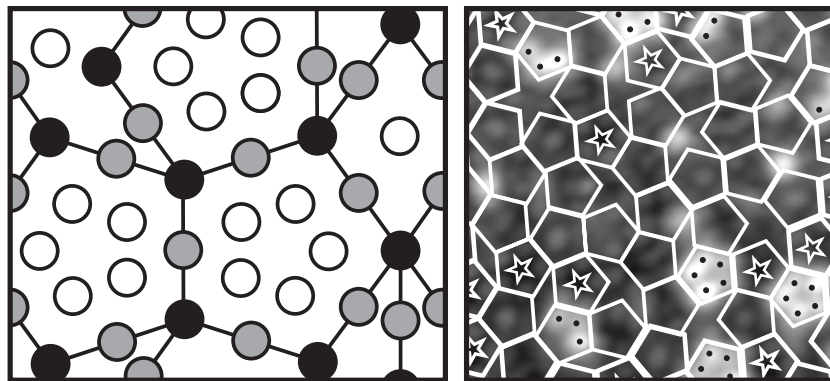
Figure 4. Left: the adsorption site network predicted for i-Al–Pd–Mn/Bi using DFT. The dark circles have the highest expected binding energy, after [33]. Right: the observed distribution of pentagonal clusters. The white protrusions are Bi atoms. A Penrose tiling of edge length 7.8 Å has been superimposed on this image. Clearly identified pentagonal hollows are indicated by pentagram motifs. The pentagonal clusters are contained within one orientation of pentagonal tiles corresponding to truncated pseudo-Mackay clusters with a Mn atom at their centre [35]. The image size is approximately 80 Å × 80 Å.

technique is capable of providing exclusive information of the top-most layer because He atoms reflect well above the surface. The diffraction patterns from the surface at monolayer coverage showed symmetry and peak positions identical to those from the respective clean surfaces, revealing the fivefold quasicrystalline structure of the monolayers.

Here we focus only on those results pertaining to Bi on the fivefold surface Al–Pd–Mn. The diffusivity of the Bi adatoms was analysed by measuring the change in the specular (reflected) intensity of He atoms during deposition at a constant flux. At a deposition temperature of 423 K, the intensity variation at sub-monolayer coverage was found to exponentially decay, suggesting a random distribution of the adatoms (i.e., no island formation).

The monolayer was found to be stable up to high temperatures (673–873 K), indicating a strong covalent bond between the adatoms and substrate atoms. Bonding to Al atoms was suggested by several observations. Firstly the density of the Bi monolayer was estimated to be $(0.9 \pm 0.2) \times 10^{15}$ cm^{-2}. This value is very similar to the density of Al atoms in the top-most layer of the substrate [32]. Secondly, the monolayer was found to be inert to adsorption of residual gases in the experimental chamber, while the clean surface, which is Al-rich, is quickly contaminated. This suggests the saturation of all Al atoms at the surface. Finally, the monolayer showed a corrugation higher than that of the clean surface. This could be due to the covalent nature of Al–Bi bonds.

An attempt was made to replicate these experimental results theoretically [33]. Krajčí *et al* used a 2/1 approximant to model the fivefold i-Al–Pd–Mn surface to find the nucleation sites for adsorbing Bi atoms. These approximants are discussed in detail elsewhere [34]. The binding energies for a Bi atom were calculated at specific points on the surface and were used as a basis for the initial positions of Bi atoms for a full monolayer relaxation. The simulations were carried out at 0 K. The suggested sites for the most tightly bound atoms of the Bi monolayer were at the vertex sites of a Penrose P1 tiling with an edge length of 7.76 Å (see figure 4 (left)). Atoms halfway along each edge of the tiling were also predicted to

be quite stable, with the remaining atoms forming smaller pentagons inside the pentagonal tiles of the tiling. The vertices of the tiling are mostly located at Pd atoms 0.48 Å below the surface—the B clusters. The Bi monolayer constructed in this way displays pseudodecagonal symmetry.

A further experimental study has been undertaken using STM [35]. In that work, the quasicrystalline monolayer was found to form via the initial adsorption of a dispersed network of pentagonal clusters of edge length 4.9 ± 0.1 Å followed by space-filling until a complete monolayer is formed, in a manner very similar to that reported for Pb [21]. At higher coverages, three-dimensional growth occurs; crystalline Bi islands with well-defined edges and magic heights decorate the surface. Due to the high resolution obtained simultaneously of both adsorbate and substrate, identification of the nucleation sites was possible.

Following the DFT work of Krajčí and co-workers on the clean surface [36], a Penrose P1 tiling was used as an analysis tool. The pentagonal clusters of Bi at low coverage never occupy a pentagonal hollow, but are always adjacent to at least one of these features. Applying the tiling technique to images of low Bi coverage, the pentagonal hollows were enclosed in pentagons of edge length 7.8 Å. It was found that complete Bi clusters always occur in pentagons of the opposite orientation as shown in figure 4. The number density of pentagons of each orientation in an infinite Penrose tiling is approximately 36% [37], and the surface area occupied by each orientation of pentagon is therefore >40%. With reference to the simulated STM data of [36], it was deduced that the pentagons occupied by the Bi clusters enclose equatorially truncated pseudo-Mackay clusters, and hence Mn surface atoms are at the centres of the adsorption sites for pentagonal Bi clusters [35]. The Bi adatoms themselves were each postulated to bond to three substrate atoms within these pentagonal tiles, the majority of which were Al.

There are points of agreement and disagreement between all these studies. The STM results indicate a fivefold monolayer, in agreement with the LEED/HAS study but in contradiction to the DFT work. The initial nucleation site
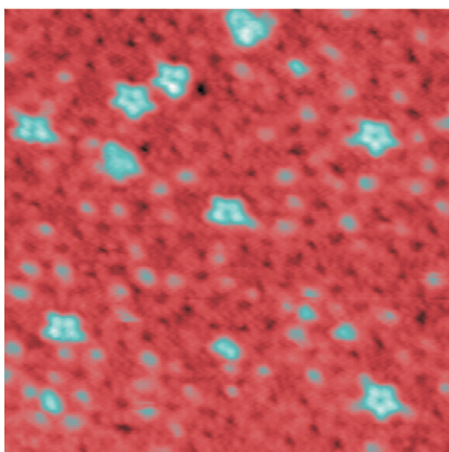
Figure 5. STM image (100 Å × 100 Å) of Al deposited on the fivefold surface of i-Al–Cu–Fe at a coverage of 0.04 ML. Reprinted with permission from [27]. Copyright 2003 by Elsevier.

determined using STM is in contradiction to that proposed using DFT. These results suggest that the DFT calculations should be refined. The HAS deduction of a random distribution of adatoms is contradicted by the STM observation of pentagonal clusters.

2.5. Al adsorption on the 5-f Al–Cu–Fe surface

Aluminium atoms adsorbed on the fivefold surface of i-Al–Cu–Fe at low sub-monolayer coverages (0.04 ML) are observed using STM to form fivefold pentagonal clusters which were dubbed 'starfish' [27]. These are illustrated in figure 5. This was the first real-space evidence for pseudomorphic motifs on a quasicrystalline substrate.

The distance between the atoms in the 'legs' of the starfish was measured at 5.1 ± 0.2 Å. The height of the legs of the starfish above the substrate was measured using line profile analysis to be 2.5 Å. The starfish were found to form independent of the incident flux, which according to the theory of nucleation and growth is indicative of adsorption on specific surface sites of fixed density. Upon further deposition, the starfish do not grow laterally but vertically. This was

postulated to be due to the low surface energy of the underlying substrate.

Preferred nucleation sites were identified by inspection of several terminations of the Boudard model [38]. The common orientation of the starfish, and their lateral dimension, led to the suggestion of certain fivefold symmetric sites bounded by Al atoms forming a pentagons of edge length 4.695 Å. It was further postulated that the central vacancy was critical to the adsorption process. The proposed nucleation mechanism involving the trapping of a single Al adatom in the centre of the vacancy which then acted as a nucleation site for the adsorption of further adatoms (although it was noted that this central Al atom was not observed unambiguously in STM).

The formation and stability of these clusters was later investigated in detail using a kinetic Monte Carlo simulation [29, 39]. Calculations were made of adsorption site binding energies and activation barriers of Al adatom hopping. These calculations, coupled with the modelling of deposition and diffusion processes, supported the interpretation suggested by the STM experiments.

2.6. Sn adsorption on the 5-f Al–Cu–Fe surface

The growth of Sn on the fivefold i-Al–Cu–Fe surface was investigated by STM. The deposition was carried out at an elevated substrate temperature of 573 K and STM images were recorded after the sample was cooled down to room temperature. An STM image at monolayer coverage is shown in figure 6. The deposited Sn forms a smooth film of monoatomic height (1.5 Å from the substrate, which is consistent with one-half of the lattice constant of tetragonal Sn) [40].

The analysis based on the Fourier transform and autocorrelation functions derived from high resolution STM images reveals that the film is quasicrystalline. The film consists of fine structure (grey parts), protrusions (representatives are marked by black circles) and pentagonal depressions marked by squares. The protrusions and depressions yield areas of local pentagonal symmetry (marked in figure 6).

A number of observations suggest that the protrusions are adsorbed in a ring of pentagonal hollows of the
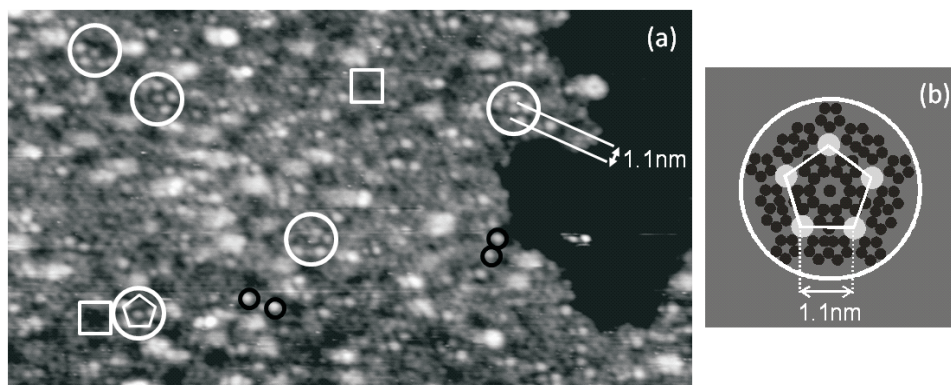

Figure 6. (a) STM image of the fivefold surface of i-Al$_{63}$Cu$_{24}$Fe$_{13}$ after deposition of a monolayer of Sn (450 Å × 250 Å). (b) Illustration of possible locations for Sn protrusions (grey circles), where substrate atom sites are represented by black dots, after [40].
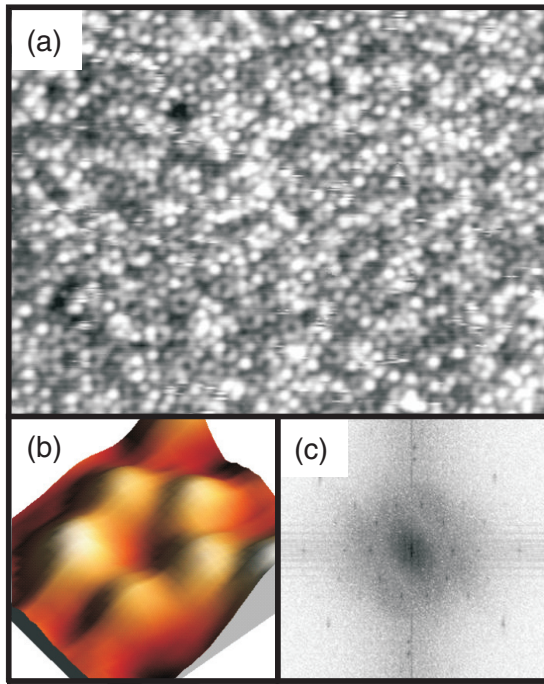
Figure 7. (a) STM image (400 Å × 310 Å) of the fivefold Al$_{63}$Cu$_{24}$Fe$_{13}$ surface dosed with 0.35 ML of Bi. (b) 3D view of a local pentagonal motif formed by 5 Bi adatoms (29 Å × 29 Å). (c) Fast Fourier transform of the image in (a). Reprinted with permission from [41]. ©(2005) the American Physical Society.

Figure 8. 80 Å × 80 Å STM image of 0.30 ML of Si adsorbed on the tenfold surface of d-Al–Ni–Co. Two Si pentagonal structures of opposite orientation are highlighted. The centres of the protrusions along the line indicated are 4.2 Å apart. After [42].

substrate, corresponding to truncated Bergman clusters or surface vacancies [36] (the point of the identification of these pentagonal hollows is discussed further in section 3.1). First, the nearest and next-nearest neighbour distances of the protrusions are 1.1 ± 0.1 nm and 1.8 ± 0.1 nm (=τ × 1.1) nm. The distances between the substrate pentagonal hollows are identical to these values. Second, the lateral size of the protrusions roughly matches the size of the pentagonal hollows. Third, the pentagonal assembly formed by the protrusions (marked by white circles) is identical to that of the substrate hollows as shown in figure 6(b) (with the addition of a protrusion in the centre). Fourth, the density of the pentagonal assemblies differs on different terraces; this is also the case for the substrate hollows. It is unknown whether the protrusions comprising the 'legs' of the cluster are single atoms or not.

With increasing coverage, Sn develops three-dimensional islands [40]. The lateral size, density, and height of the islands vary from terrace to terrace. The islands tend to adopt the height of the substrate steps.

2.7. Bi adsorption on the 5-f Al–Cu–Fe surface

The growth of Bi on the fivefold i-Al–Cu–Fe surface was investigated by STM [41]. A wetting layer was formed first, followed by the growth of large Bi islands for larger coverages. Figure 7 shows an STM image (400 Å × 300 Å) of a single terrace of the surface dosed with approximately 0.35 ML of Bi. It is partly covered with dots of bright contrast that correspond to isolated Bi adatoms. The structure of the Bi wetting layer was interpreted to be quasiperiodic. Local
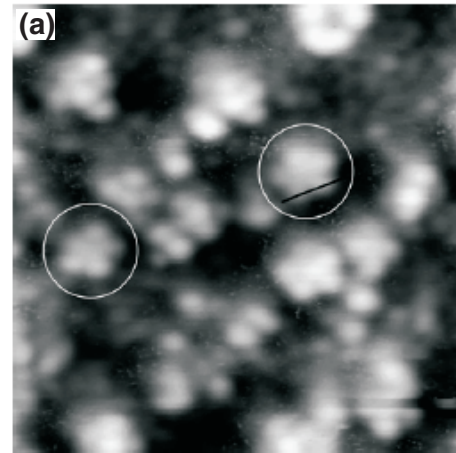
configurations of Bi atoms with pentagonal symmetry were frequently observed (figure 7(b)). The distance between Bi atoms in these configurations was 6.9 Å, and the FFT of the STM image yields a tenfold symmetric pattern (figure 7(c)). By applying an appropriate height threshold to the raw STM image, it was also possible to generate a binary image where dots reflect the positions of Bi adatoms. The FFT of this image still showed the tenfold symmetry. At coverages greater than 1 ML, islanding occurs. Above monolayer coverage, the growth proceeds as Stransky–Krastanov, with the formation of magic height islands on the surface [41].

2.8. Si adsorption on the 10-f Al–Ni–Co surface

Upon initial adsorption of Si on the tenfold surface of d-Al–Ni–Co, a variety of adsorbed features are observed [42]. With reference to figure 8, the formation of individual pentagonal structures as well as the adsorption of single atoms is observed. This indicates the absence of a unique nucleation site. The pentagons are related by inversion symmetry and the sides of the pentagons are aligned along high symmetry directions of the substrate. The pentagons appear to consist of six atoms, with five atoms forming the 'arms' of the pentagon and a sixth atom in a central position. The distance between atoms in the 'arms' of the pentagon is 4.2 ± 0.2 Å.

To establish the long-range arrangement of the Si atoms at this coverage, a height filter was applied to an image to remove any influence of the substrate structure. The application of a fast Fourier transform (FFT) to the data yields a tenfold pattern. This indicates that at this coverage, quasiperiodic ordering of the Si atoms/clusters exists.

Further adsorption to a coverage of 0.75 ML leads to the disappearance of the LEED pattern. Following completion of the monolayer, the film grows in a three-dimensional nature.

2.9. Pb adsorption on the 10-f Al–Ni–Co surface

Pb deposited on d-Al–Ni–Co forms a quasicrystalline pseudomorphic monolayer [43]. On the surface of d-Al–Ni–Co,

Table 1. A list of experimentally determined parameters for pseudomorphic adsorbed overlayers as discussed in section 2. All of the parameters were derived using STM studies. Truncated M refers to an equatorially truncated pseudo-Mackay cluster. The numbers is column 5 refer to the distances in Å between protrusions in the 'legs' of the pentagonal clusters.

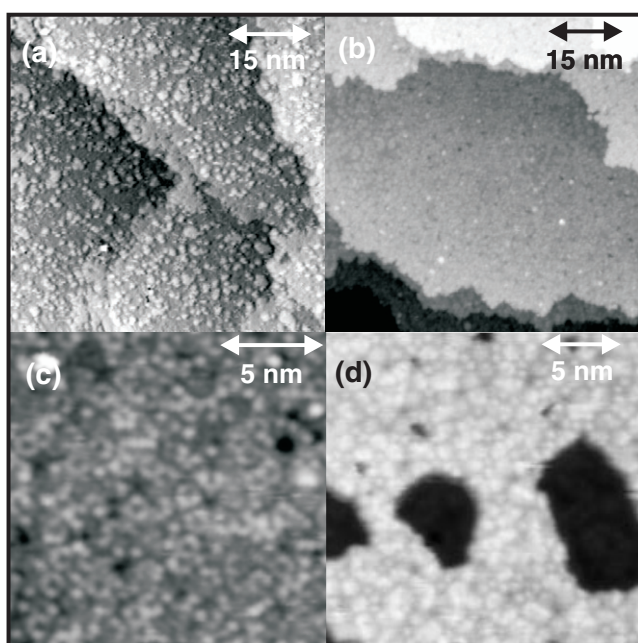| Substrate	Adsorbate	Pseudomorphic monolayer	Suggested site	Pentagonal cluster	Ref.
i-Al–Pd–Mn	C_{60}	—	Hollow	—	[18]
	Si	—	Truncated M	—	[44]
	Pb	✓	—	4.9	[21]
	Bi	✓	Truncated M	4.9	[31, 35]
i-Al–Cu–Fe	Al	—	Hollow	5.1	[27]
	Sn	✓	Hollow	11.0	[40]
	Bi	✓	—	6.9	[41]
d-Al–Ni–Co	Pb	✓	—	—	[43]
	Si	—	Hollow	4.2	[42]

Figure 9. STM images of the formation of the Pb film on d-Al–Ni–Co. (a) 570 Å × 570 Å, 0.32 ML; (b) 640 Å × 640 Å, 1 ML; (c) 150 Å × 150 Å, 1 ML, showing structural motifs associated with quasicrystalline ordering; (d) 200 Å × 200 Å following annealing to 600 K, showing the porosity developed in the film.

it appears that Pb is very mobile, with large islands forming which have noise at the edges associated with the movement of the less coordinated Pb atoms by the STM tip. XPS measurements indicate that the chemical interaction of the Pb atoms with the substrate is weak. The islands mostly nucleate at step edges, presumably because of the increased coordination, and are indistinguishable from the existing d-Al–Ni–Co planes by STM, primarily because the island height is equivalent to the step height for clean d-Al–Ni–Co. These islands ultimately coalesce to form an extended, well-ordered monolayer. As for the case for i-Al–Pd–Mn, the sticking coefficient of Pb drops to zero as full monolayer coverage is attained. Figure 9 follows the growth of the film.

When the i-Al–Pd–Mn/Pb film is annealed to 673 K, the surface order improves dramatically. When the d-Al–Ni–

Co/Pb film is annealed to 600 K, nanosized 'pores' develop at the surface. However, the perfection of the structure at the surface is greatly improved. The material inside the pores appears to have the structure of the surface layer rather than that of the underlying d-Al–Ni–Co/Pb substrate and as for the unannealed film, no more Pb may be deposited. The step height of the pore walls is the same within experimental error to the step height of the d-Al–Ni–Co substrate (2.1 ± 0.1 Å), and is thus consistent with the Pb islands in the sub-monolayer film, though significantly lower than the step height of close-packed Pb (2.86 Å).

3. Discussion

3.1. General remarks

Table 1 summarizes the structural information deduced for the systems under consideration in this paper. To begin with, we first address a number of limitations apparent from this exercise.

Firstly, overall there is a paucity of information. The number of systems studied where adsorption information has been deduced is small. There is slightly more information available for fivefold icosahedral surfaces than for the tenfold decagonal ones; however, there is no information for twofold or threefold surfaces. Secondly, the information above on the adsorption and nucleation sites is semi-quantitative. None of the studies listed in table 1 would satisfy the criteria for entry to the NIST Surface Structure Database [45], which is an authoritative collection of the surface/adsorbate systems studied to date using quantitative techniques.

Thirdly, while the assignment of adsorption/nucleation sites on icosahedral surfaces on the basis of STM measurement to pentagonal hollows or to truncated pseudo-Mackay clusters seems relatively robust, there is currently uncertainty about the origin of the pentagonal hollows themselves. On the basis of a comparison of bulk 'ball and stick' models, these features were first assigned to truncated Bergman clusters [12, 22]. However Krajčí and co-workers have shown, using density functional theory simulations of STM images, that such features can result from particular truncations of pseudo-Mackay clusters [36] leading to surface vacancies. In the termination studied by Krajčí (the 'R' termination in the language of [22]), there were

no such truncated Bergman clusters; and it was pointed out that DFT STM simulations of terminations containing such Bergman clusters should be undertaken to see if they do in fact produce these pentagonal hollow features [36]. This issue has also been commented on by Thiel [46].

Nevertheless it is clear from table 1 that from a situation a few years ago where no pseudomorphic growth had been observed, it is now apparent that such behaviour is not uncommon, at least in certain chemically similar adsorbates. The question of which elements form such systems has been addressed by us elsewhere [7].

The question of whether pseudomorphic behaviour is possible beyond monolayer coverage is an open one. It has not been observed to date in those systems which do form pseudomorphic monolayers: for Pb adsorption on i-Al–Pd–Mn [21] and d-Al–Ni–Co [43] the coverage saturates at a monolayer. For Sn on i-Al–Cu–Fe three-dimensional growth occurs [40], while for i-Al–Pd–Mn/Bi, further adsorption leads to the formation of magic height crystalline Bi islands (which were also observed for i-Al–Cu–Fe/Bi [41]). Pseudomorphic growth of thin films has been observed to take place in heteroepitaxial systems where there is a small lattice mismatch, e.g. Fe/Cu(100), where bcc Fe is not observed until about 12 ML thickness [47]. It is not known whether similar behaviour can be observed in a quasicrystalline system, although there would not appear to be any fundamental reason why not. Krajčí and Hafner have concluded from a DFT study of alkali adatoms on i-Al–Pd–Mn that a quasiperiodic bilayer should be possible, although with for three or more layers, the adatoms relax into a disordered amorphous arrangement [48].

3.2. Criteria for pseudomorphic monolayer growth

We now turn to the question of what is necessary for the growth of a pseudomorphic monolayer. Looking first at those systems where pseudomorphic monolayers are grown it is apparent that a number of criteria must be met in order for pseudomorphic growth to occur, at least on fivefold icosahedral surfaces.

 (i) It seems that a unique adsorption/nucleation site is initially occupied, for example as evidenced by the pentagonal clusters observed for Pb [21] and Bi [35] on i-Al–Pd–Mn and for Bi on i-Al–Cu–Fe [40].
 (ii) There must be a sufficient density of sites to allow a framework or skeleton to develop as coverage increases. In the case of Bi, where the site was identified as the equatorially truncated pseudo-Mackay cluster, it is estimated that >40% of the area of the surfaces is taken up by such features on an 'R' termination [35]. Thereafter, additional atoms can be added to the basic structure (at lower binding energy sites) until a monolayer is completed. This interpretation is also supported by those cases where pseudomorphic growth does occur at sub-monolayer coverages, but does not result in a pseudomorphic monolayer. This is the case for Al adsorption on i-Al–Cu–Fe, where adsorption does take place in a well-defined site [27]. There is some indication that this also applies to the case of Si adsorbed on d-Al–Ni–Co [42].

(iii) Provided the above criteria are satisfied, a third criterion appears to be important: that the adsorbate atoms should form a pentagonal cluster. For example, in cases where the first two criteria are met but the atom or molecule adsorbs as a single entity, the adsorbates appear to be too widely dispersed on the surface to form a framework. This was the case for both C_{60} and Si adsorbed on i-Al–Pd–Mn.

The question of why pentagonal clusters form is an interesting one. In general, as can be seen from table 1, although there are exceptions, there is some tendency for clusters to form where the atom–atom distance is ∼4–5 Å. This is too large for a chemical bond, and suggests the clusters nucleate around a particular atom. In the case of i-Al–Cu–Fe/Al, it was suggested that there is a central Al atom which acts as a nucleation site for the other five atoms [27, 29, 39]. For Bi on i-Al–Pd–Mn, it was noted that a substrate Mn atom is present in the centre of the proposed adsorption site [35]. The presence of this Mn atom, which is thought to have a large negative valence [49, 50], could have an influence *via* a substrate-mediated interaction.

With regards to the actual chemical environment of the adsorbing atoms, for the most part the techniques that have been utilized (HAS, STM, LEED) yield no information. The application of XPS to Pb adsorption on both i-Al–Pd–Mn [21] and d-Al–Ni–Co [43] was inconclusive: in neither case were any chemically shifted core levels observed, either for the adsorbate or the substrate.

On decagonal surfaces the growth mechanism of a pseudomorphic monolayer is less clear. For the case of Pb, for example, although a pseudomorphic monolayer is clearly observed [43], at sub-monolayer coverages there was no indication of pentagonal clusters as an element in the building of a quasiperiodic framework using STM, despite the fact that two orientations of such clusters were observed in Si adsorption on this surface [42].

3.3. Application of quantitative surface structural techniques

Adsorption on crystalline surfaces have been studied quite extensively over the past thirty years. A number of specialized experimental techniques have been developed specifically to address the question of adsorption site determination.

In the LEED intensity–voltage ($I(V)$) technique diffraction intensities calculated from model structures are matched to measured spot intensities in order to refine the structure and hence deduce the adsorption site. Progress has been made on the LEED analysis of clean quasicrystal surfaces by implementing several approximations. Examples include the fivefold surface of Al–Pd–Mn [32, 51] and the tenfold surface of Al–Ni–Co [52]. Current work centres on the use of approximants as model systems for the modelling of data from quasicrystalline surfaces [53]. Adsorption site and overlayer structure determination using LEED $I(V)$ has not been accomplished at present. The overlayer must of course have measurable diffraction intensity; therefore diffraction is not applicable to low sub-monolayer coverages. It is feasible however that the structure of monolayer coverages could be solved using this methodology. Another diffraction technique, surface x-ray diffraction

(SXRD) can also be utilized. However although the modelling of SXRD data is in principle simpler than that of LEED data, as single scattering of electrons can be assumed, there is limited experience of the solution of clean surface structures using this technique [54, 55].

Techniques are available that probe the local structure around an adsorbate without the requirement of long-range order. These include surface x-ray absorption fine structure (SEXAFS) and photoelectron diffraction (PhD). These techniques which provide direct information on the adsorption site can be applied at low coverages provided that a high intensity synchrotron radiation source is used. Application of the technique to sub-monolayer coverages of Bi or Pb adsorbed on i-Al–Pd–Mn could provide quantitative confirmation of the suggested adsorption site. Similarly PhD monitors the local geometry round an adsorbate. These local techniques work best if a unique adsorption site is occupied.

The normal incidence x-ray standing wave (NISXW) technique has been applied to bulk i-Al–Pd–Mn [56]. In principle by measuring the position of adsorbates relative to bulk planes the coordinates may be triangulated. However the need for a detailed knowledge of which bulk planes give rise to reflections, and the difficulty of assigning inter-planar spacings makes the application of this technique to quasicrystal adsorbate systems difficult. Finally medium energy ion scattering (MEIS) has been applied to the clean surface of i-Al–Pd–Mn [57] and to thin films of Au [58] and Cu [59] on the same surface. In principle this could be applied to monolayer and even sub-monolayer coverages.

4. Summary

We have surveyed the experimental information available on pseudomorphic monolayers and adsorption/nucleation sites on quasicrystal surfaces. A clear picture of growth of a pseudomorphic monolayer on icosahedral surfaces emerges. Unique adsorption/nucleation sites of sufficient density are necessary in the initial stages of growth. Nucleation at these sites of pentagonal clusters allows the formation of a quasicrystalline framework; additional atoms in the interstices of this framework complete the monolayer while maintaining quasiperiodic order. Although the picture is not as clear for decagonal surfaces, a similar mechanism can be envisioned. The need for quantitative measurements has been highlighted and the suitability of several quantitative surface structural techniques has been discussed.

Acknowledgments

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