CLUSTERED, TERRACED AND MIXED SURFACE PHASES OF THE $Al_{70}Pd_{21}Mn_9$ QUASICRYSTAL

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ABSTRACT

The five-fold surface of the $Al_{70}Pd_{21}Mn_9$ quasicrystal has been studied using STM, LEED and AES. STM images from surfaces which have been sputtered and annealed to 875 K reveal 20-30 Å protrusions that have been identified by others as Mackay-type clusters. Higher-resolution images reveal substructures in these clusters having dimensions 2-3 Å. Longer annealing times at 875 K produced large areas having flat terraces which were imaged with atomic resolution. The LEED pattern from this surface has sharp spots on a low background, and AES indicates that the surface is deficient in Mn relative to the bulk. For surfaces annealed to 1050 K for less than 2 hours, STM images indicate that cluster and terrace phases coexist, and a third phase having aligned arrays of clusters is identified which appears to be intermediate between the cluster and terrace phases.

INTRODUCTION

The unusual surface properties of quasicrystals, which include low coefficients of friction under certain conditions compared to steels and Al alloys [1] as well as their surface energies which may produce a "non-sticking" behaviour [2] and in their oxidation resistance. Recently, the growth of large single grain samples of the icosahedral $Al_{70}Pd_{21}Mn_9$ has facilitated studies of this surface using Scanning Tunnelling Microscopy (STM) [3-10], Low Energy Electron Diffraction (LEED) [11-13] and X-Ray Photoelectron Diffraction (XPD) [14-16].

A consensus has developed for the structure of the five-fold $Al_{70}Pd_{21}Mn_9$ surface after it has been cleaned by sputtering and annealing. For annealing to 875 K or less, a rough clustered surface is observed, having clusters of 20-70 Å diameter [3-6, 10]. This surface is similar to that obtained by cleaving [8, 9] and has been interpreted on the basis of an elementary cluster (diameter 9.6 Å) which is consistent with a Mackay-type cluster [8, 9].

For annealing to higher temperatures (1050 K), STM studies have identified a flat terraced phase [3-7, 10]. The STM studies of this flat terraced phase by Schaub *et al.* [3-6] have provided an interpretation in terms of a Fibonacci pentagrid. Shen et al. showed that the surface structure is consistent with a bulk structure based on Pseudo-Mackay Icosahedra [7]. Ledieu *et al.* [10] pointed out similarities to the theoretical surface tiling model of Janot [17], with frustration in the tiling correlating with the presence of large defect peaks. A dynamical LEED analysis by Gierer *et al.* indicates that this five-fold surface is consistent with the bulk quasicrystal structure of $Al_{70}Pd_{21}Mn_9$ [11, 12]. Finally XPD studies are also consistent with a quasicrystalline surface nature [14-16], though these workers report that annealing as high as 1025 K results in a cubic Al-Pd surface alloy with a stoichiometry different from the flat-terrace phase.

Here we report on our investigation of both clustered and flat *i*-$Al_{70}Pd_{21}Mn_9$ surfaces. For the clustered surfaces our STM images reveal a hierarchy of clusters with a basic structure of diameter 2- 3 Å. Images of the flat surface are consistent with those reported by previous workers. We also show images which show the coexistence of the flat and clustered phases, together with a third 'intermediate' phase which may be transitional between the two well-established phases.

EXPERIMENTAL DETAILS

The quasicrystal sample was grown by the Ames Laboratory group [18, 19] using the Bridgman method. This *i*-$Al_{70}Pd_{21}Mn_9$ sample consists of a slab (18x18x2 mm^3) cut perpendicular to its five-fold symmetrical axis under atmospheric pressure. Before being inserted in the UHV chamber the sample was polished with a 1/4 micron diamond paste on Texmet cloth for one hour. The surface was then mirror-like. It has been noticed that after several cycles of annealing the surface changes to a matt appearance due to partial desorption of surface layers [9]. The measurements of temperature were done using an optical pyrometer with emissivity optimised for Al. This introduces an error of ± 30 K in the temperatures quoted. The preparation of the quasicrystal consisted of cycles of argon ion sputtering at 1 KeV (7 μA) and annealing for several hours. All the data were taken in UHV with a pressure of 5×10^{-11} mbar. The LEED patterns were recorded after each cycle, and the surface was investigated using an Omicron STM at different places across the whole width of the surface in order to check the uniformity of the cleaning process. The Auger scans were obtained using a Perkin-Elmer double pass cylindrical mirror analyser (model 15-255G) in a separate UHV chamber, but following exactly the preparation sequence used for the STM measurements.

RESULTS

The clustered phase

After being at atmospheric pressure for a long time a thick aluminium oxide layer covers the whole surface of the sample [20]. Therefore we sputter the quasicrystal at 1 KeV with Ar^+ ions for 90 minutes at 5×10^{-5} mbar. The Auger scan reveals a surface stoichiometry estimated at $Al_{43.9}Pd_{52.6}Mn_{3.5}$ (estimated errors in the stoichiometry are ± 3%) and matches with the composition measured by Naumovic' *et al.* [14-16]. A five-fold symmetric LEED pattern is obtained after annealing the sample to 870 K for 2 hours 30 minutes. Five relatively sharp spots are observed as first order peaks and ten other spots as a second set of reflections (Fig. 1(a)). The quality of the LEED pattern degrades somewhat as the sample cools (higher background). The distances from

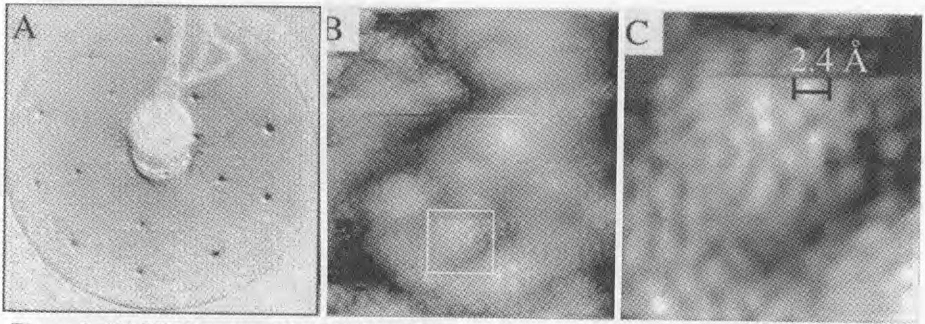

Figure 1: (A) LEED pattern (inverted for clarity) obtained after annealing to 875 K at 78.9 eV. (B) 100 x100 Å ^{2}- sized high resolution STM image corresponding to the clustered phase (bias voltage -1.07 V, tip current 1.07 nA). (C) 25 x25 Å ^{2} region of the STM image shown on (B).

the centre are related by powers of the irrational Golden mean τ (=1.618...) as demonstrated by Guyot and co-workers [13]. AES exhibits a relative composition of the three compounds of the top layer of $Al_{72.6}Pd_{24}Mn_{3.3}$.

At this stage STM images show a rough surface and reveals cluster-like protrusions (Fig. 1(b)). Features of diameters between 20 Å and 30 Å can be recognised. Higher resolution scans show substructures of diameters close to 2 Å-3 Å (Fig. 1(c)). These substructures look identical to those obtained by Ebert *et al.* [9], for surfaces obtained by cleaving and subsequent annealing to 870 K. In contrast, surfaces cleaved and imaged at room temperature have a smallest substructure of diameter 9 Å [8,9]. This led to a model for the structure of a hierarchy of clusters based on a pseudo Mackay unit [8,9]. The Mackay cluster is an icosahedron of 12 spheres about a central sphere surrounded by another icosahedral shell formed by 42 other spheres; the pseudo Mackay Icosahedron is an adaptation of the Mackay cluster and contains 51 atoms made of an inner small centered cubic core of 9 atoms, an intermediate icosahedron of 12 atoms, and an external icosidodecahedron of 30 atoms having an overall diameter of 9.6Å [21]. It is possible that the high resolution image in Fig. 1(c) is of atomic resolution; however the STM does not provide chemical sensitivity so that it is difficult to suggest structural correspondence with pseudo Mackay clusters based on these data.

The flat terrace phase

Argon ion bombardment for one hour at 1KeV resets the composition of the surface as it was before the preparation of the clustered phase ($Al_{43.9}Pd_{52.6}Mn_{3.5}$). Then annealing to 1050 K for 2 hours changes the stoichiometry of the surface region to $Al_{74.6}Pd_{21.7}Mn_{3.7}$ as determined by AES. The LEED pattern taken from this preparation is very sharp and exhibits a low background, sharp peaks and ten-fold rotational axes (Fig.2 (a)). Extra spots appear between the principal peaks. Using the STM, flat terraces are revealed and high resolution images from the surface were ob-

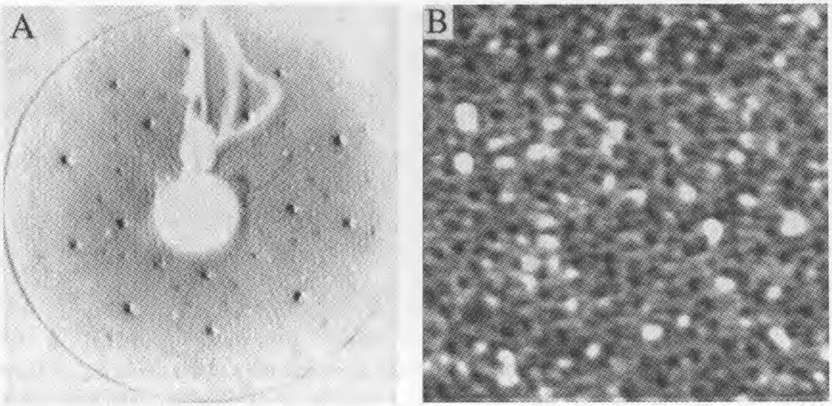

Figure 2: (A) LEED pattern (inverted for clarity) recorded after annealing to 1050 K at 83.7 eV. (B) High resolution inverted (200 x 200 Å ^{2}) STM image of a flat terrace (bias voltage 2.29 V, tip current 0.59 nA).

served (Fig. 2 (b)). The visual appearance of the surface is now matt as reported before [9].

In previous work we showed that this surface may be tiled using a thresholding analysis for pattern recognition [10]. A random tiling with pentagons (median length 16 ± 0.2 Å) generated by pentagonal holes presented similarities with the random tiling model described in [17].

Coexistence of two phases

Here we report the coexistence of the clustered and flat terrace phases. If, after sputtering the sample for one hour, the sample is annealed to 1050 K for a period less than two hours, a coexistence of the cluster phase and the terrace phase is observed. STM scans show flat terraces on the left hand side of the sample while the right hand side exhibits a mixture of cluster-like protrusions and atomically flat terraces. The diameters of the clusters obtained are estimated between 20 Å and 60 Å, similar to our previous measurements of the cluster phase [10]. The different regions labelled on Fig. 3(a) appear to represent three stages in the cluster to terrace transition. Clusters are shown in contact with the terrace phase. Additionally clusters on region 2 tend to appear to align in a preferential direction. This feature is shown more clearly on Fig. 3(b).

These results can be compared with those of Ebert *et al.* for annealing of a cleaved sample to 850 K for ~2 hours [9]. Here some parts of the surface remained cluster-like while on other parts holes were observed to form, depending on the local starting composition. These holes were interpreted as due to preferential desorption of material from the surface eventually resulting in a flat terrace phase.

Our coexisting cluster and terrace phases were observed after annealing to some 200 K higher temperature than this and from a sputtered rather than a cleaved starting surface. We also

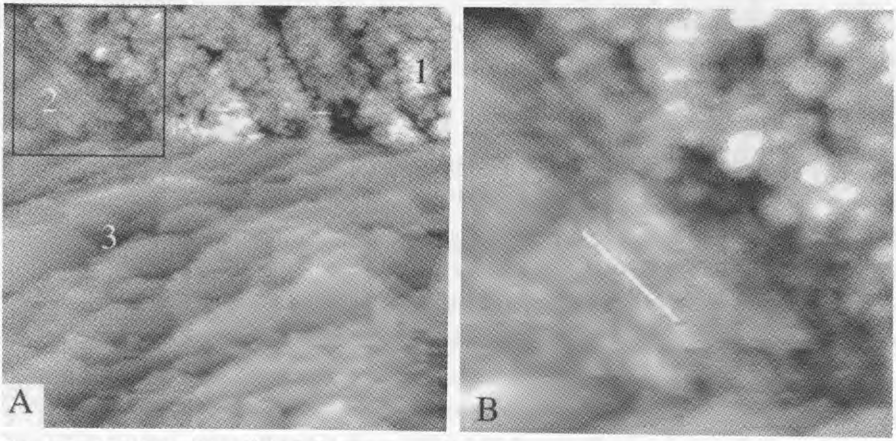

Figure 3: (A) 2000 x 2000 Å ^{2} STM image revealing the coexistence of the clustered and terrace phases (bias voltage 1.0 V, tip current 1.0 nA). A line by line quadratic compensation is applied to the image. (B) 600 x 600 Å ^{2} STM image of the framed area in (A) showing the preferential alignment of clusters/cluster fragments in region 2 (bias voltage 1.0 V, tip current 1.0 nA).

observed differences in the structure in different parts of the sample as described above which could be due to a temperature gradient across the sample. We do observe a third region where it looks as if some clusters are being removed or fragmented; the residues appear to align along specific directions in the surface, and the whole surface eventually becomes flat if annealed for long enough. Our AES results from the cluster and terrace phases show a close but not identical stoichiometry, so that slight preferential desorption of material may be occurring as was suggested for the data in ref. [9].

SUMMARY

For surfaces annealed to 870 K for several hours, the surface is found to be rough and is consistent with a hierarchy based on the Pseudo-Mackay Icosahedron (PMI). STM images showed substructures with diameters of 2 - 3 Å. At this stage the surface is Mn deficient and Pd rich. Annealing the sample to 1050 K for more than two hours gives rise to flat terraces and a very sharp LEED pattern as expected. The surface stoichiometry is then Al rich. Annealing the surface to 1050 K for less than two hours leads to the coexistence of the clustered and terraced phase. Additionally, after this annealing procedure, a third topography has been distinguished and corresponds to alignment of clusters or cluster fragments in a preferential direction. This 'intermediate' phase may represent the transition between the clustered and terraced phase.

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