Structure and Stability of the Twofold Surface of Icosahedral Al-Pd-Mn by Low-Energy Electron Diffraction and X-Ray Photoemission Spectroscopy

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We have used low-energy electron diffraction and x-ray photoemission spectroscopy to investigate the structure of the twofold surface of icosahedral Al-Pd-Mn. The regrowth of the surface by annealing after sputtering took place in two distinct stages. The first stage was the appearance of a fine-grained surface phase with icosahedral, or near-icosahedral, symmetry. For higher annealing temperatures (above 800 K) a bulk terminated face-centered icosahedral surface was observed. [S0031-9007(97)02382-X]

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With the availability of large single grains of quasicrystalline alloys, such as the icosahedral phase of Al-Pd-Mn, several experimental probes have been newly applied to the study of quasicrystalline structures. Over the past two years, the study of surface structures and chemistry by techniques such as scanning tunneling microscopy (STM) [1–5], low-energy electron diffraction (LEED) [4–7], and photoelectron spectroscopy [8,9] has emerged as one of the most active areas in quasicrystal research. The heightened interest in quasicrystalline surfaces has been motivated, in part, by reports of intriguing properties such as oxidation resistance [10–12], low surface friction [13,14], superior wear resistance, and other attractive tribological characteristics [13]. All of these properties are ultimately related to the physics and chemistry of the surface on an atomic scale. Therefore, a basic understanding of the intrinsic surface structure of quasicrystalline alloys is prerequisite to understanding how these surfaces interact with their environment.

There are some very basic issues about quasicrystalline surfaces that have yet to be resolved or even addressed. The very nature of the surfaces themselves, as well as the effects of various surface preparation techniques, are the subject of debate. For example, STM measurements on a sample of Al-Pd-Mn prepared by sputtering and annealing in ultrahigh vacuum have revealed well-defined relatively flat terraces with quasicrystalline order within the plane of the surface [2]. In contrast, STM measurements of surfaces of Al-Pd-Mn prepared by *in situ* cleavage revealed significant atomic-scale roughness [3]. These latter measurements provide some support for a cluster-based approach to quasicrystalline structure advocated by several groups in recent years [15], and have raised concerns regarding the effects of ion bombardment and high temperature annealing upon the surface since selective evaporation and sputtering can significantly change the surface stoichiometry. Indeed, as pointed out by Ebert *et al.*, quasicrystalline phases are complex chemically ordered phases whose surface structures need not be the same as in the bulk [3].

In this Letter, we directly address these issues through x-ray photoemission spectroscopy (XPS) and LEED measurements conducted on a sample of icosahedral Al-Pd-Mn oriented with a twofold axis perpendicular to the surface. After sputtering the surface with argon, no LEED pattern was observed and we found substantial depletion of the aluminum at the surface. After annealing the sample at temperatures above 800 K, a well-ordered, bulk terminated quasicrystalline surface with the same composition as the bulk was recovered. At intermediate annealing temperatures, however, the surface is best characterized as a fine-grained, nanocrystalline (or nanoquasicrystalline) precursor of the icosahedral phase. We also found that XPS measurements of the width of the Mn $2p_{3/2}$ peak can provide a good indication of the presence of the face-centered icosahedral (FCI) phase at the surface, as proposed in previous work [9].

The LEED experiments were performed in a stainless-steel ultrahigh vacuum (UHV) chamber (base pressure $< 3 \times 10^{-11}$ Torr) also equipped with provisions for Auger electron spectroscopy (AES), ion sputtering, and annealing. Supporting measurements by x-ray photoemission spectroscopy (XPS) were performed in a second chamber under the same conditions as the measurements described below, albeit at a higher base pressure (upper limit 4×10^{-10} Torr).

Our sample, a flat wafer approximately 12 mm $\times$ 15 mm $\times$ 2 mm in size, was cut from a single grain of a boule, grown via the Bridgman method [16] using a starting composition of $Al_{72}Pd_{19.5}Mn_{8.5}$, and oriented by the x-ray Laue technique so that a twofold axis was normal ($\pm 0.2°$) to the surface. Inductively coupled plasma atomic-emission spectroscopy analysis of a small piece adjacent to our sample indicated a bulk composition of $Al_{71}Pd_{19.8}Mn_{9.2}$. The phase purity was verified by scanning electron and Auger microscopies to within 0.5% by volume. For further details regarding our methods of quasicrystalline sample preparation, outside of UHV, we refer the reader to Ref. [17].

After polishing and characterization, the sample was fixed onto a thin Ta plate (20 mm $\times$ 25 mm) using two

Ta strips. The sample could be resistively heated and liquid-nitrogen cooled via the Ta plate. A thermocouple (W-5% Re/W-26% Re) was spot welded on the tantalum plate for real-time control of the sample temperature. To confirm the sample temperature measured by the thermocouple, an infrared thermometer (IR gun) was also used. The difference between the IR-gun reading of the sample temperature and thermocouple reading was less than 20 K. After initial cleaning cycles by ion bombardment and annealing, up to a maximum temperature of 900 K, LEED data at several temperature steps were taken after sputtering for 40 min at room temperature and annealing at the desired temperature for 2–4 h. Unless indicated otherwise, all of the LEED data were collected at temperatures at or below 120 K.

After sputtering, but prior to annealing at temperatures above 600 K, no LEED pattern from the twofold surface was observed. Furthermore, AES measurements indicated that the surface composition was $Al_{61\pm3}Pd_{33\pm3}Mn_{6\pm1}$, well away from both the known stoichiometry for the FCI phase of Al-Pd-Mn and the composition of the bulk sample. The shift in composition upon sputtering has been reported previously [5]. We also point out that the line shape of the Mn $2p_{3/2}$ peak measured by XPS under these conditions was quite broad (see Fig. 1). This last point is notable since recent XPS measurements on clean, well-ordered, fivefold surfaces of Al-Pd-Mn suggest that the sharpness of the Mn peak may be used as an indicator of the presence of quasicrystalline order at the surface of the sample [9]. As discussed in Ref. [9], the shape and width of the Mn $2p_{3/2}$ peak can be related to both the position and population/distribution of Mn states near the Fermi energy. Therefore, the Mn $2p_{3/2}$ peak can be a sensitive probe of the structural and chemical environment of the Mn sites in the structure.

After resputtering the sample and annealing at approximately 600 K, a LEED pattern exhibiting twofold symmetry (Fig. 2) was observed. The diffraction spots, however, are quite broad and the pattern itself clearly does not correspond to the LEED pattern expected for a bulk terminated twofold FCI surface (see discussion below). We shall refer to this pattern as “rhombic” because rhombi are apparent in the LEED pattern at certain energies as shown in Fig. 2. Twofold, threefold, and fivefold axes, corresponding to the orientation of the underlying bulk alloy, have been superimposed on the pattern in Fig. 2 in order to show that this intermediate phase is orientationally coherent with the bulk quasicrystal. The surface composition after the 600 K anneal was measured, by AES, to be $Al_{68\pm2}Pd_{27\pm2}Mn_{5\pm2}$, closer to, but still well away from, the bulk composition. Furthermore, the line shape of the Mn $2p_{3/2}$ peak, measured by XPS, under these conditions remained quite broad (Fig. 1). The breadth of the LEED spots suggests that the in-plane domain size for this phase is on the order of approximately 40 Å, so that the surface layer is best described as nanocrystalline, or, perhaps, nanoquasicrystalline [18].

After sputtering and annealing at temperatures above 800 K, the LEED pattern changed dramatically in several ways. First of all, as shown in Fig. 3(a) (taken after a 900 K anneal), the diffuse spots of Fig. 2 were replaced by a new sharp LEED pattern, also with twofold symmetry, but in a rectangular rather than rhombic pattern. In addition, faceting of the surface was observed, especially close to the edges of the sample, at temperatures above 700 K. The faceting is evidenced by Fig. 4 which shows two new $(0,0)$ spots in addition to the twofold $(0,0)$ spot (normally positioned at the center of the screen but moved here by sample rotation). The LEED patterns associated with the new $(0,0)$ beams have threefold and fivefold symmetry. We point out that the faceting observed here is consistent with a higher surface energy for the twofold surface relative to surfaces perpendicular to the threefold and fivefold directions.

After annealing the sample at 900 K the rectangular LEED pattern dominated the surface scattering except at

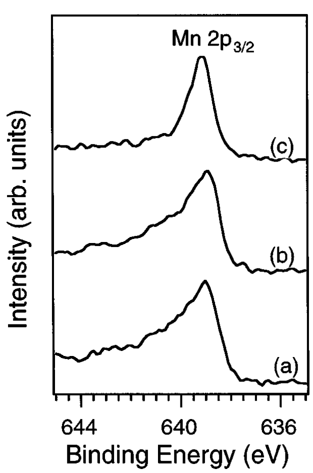

FIG. 1. XPS profiles of the Mn $2p_{3/2}$ peak for samples that were (a) sputtered and then annealed at (b) 600 K and (c) 900 K.

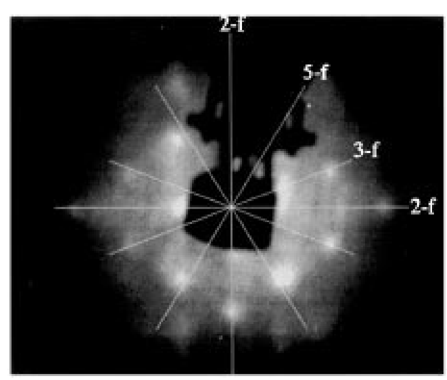

FIG. 2. LEED pattern of the rhombic phase taken at an electron energy of 110 eV. The axes denoted correspond to the twofold, threefold, and fivefold directions in the twofold plane for an icosahedral quasicrystal.

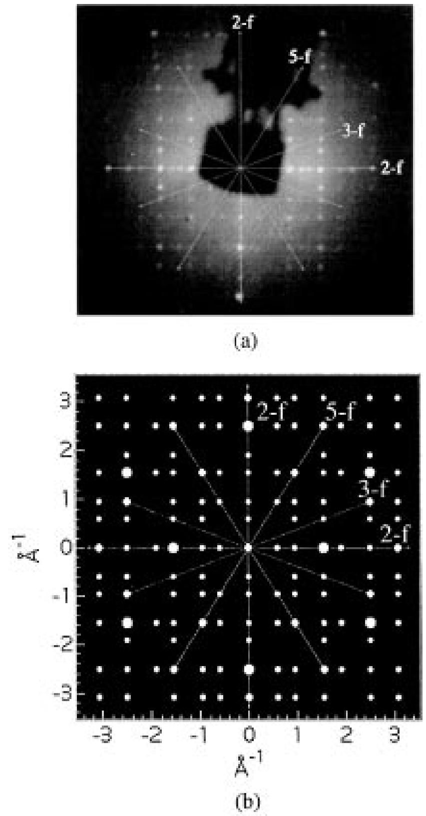

FIG. 3. (a) LEED pattern of the "rectangular" phase taken at an electron energy of 60 eV; (b) the calculated LEED pattern for an FCI surface as described in the text.

the edges of the sample. AES measurements showed that the surface composition was $Al_{73\pm2}Pd_{19\pm2}Mn_{7\pm1}$, very close to the composition of the bulk. Furthermore, XPS measurements (Fig. 1) showed that the width of the Mn $2p_{3/2}$ peak narrowed considerably, consistent with the previous measurements mentioned above. All of these results suggest that the surface layer of the Al-Pd-Mn alloy has regrown to a bulk terminated structure.

In order to confirm that the rectangular pattern is indeed characteristic of an ordered FCI surface, a LEED pattern was calculated and is shown in Fig. 3(b) [19]. To calculate the pattern we employed the bulk x-ray structure factors measured by Boudard *et al.* for Al-Pd-Mn [20], and used these to assign a relative intensity to rods of scattering parallel to the surface normal. We point out, however, that we do not expect the relative intensities of the calculated LEED spots to find very good agreement with experiment since this comparison has been made at a single LEED energy of 60 eV and, therefore, ignores structure in the surface rods. A proper comparison with experiment requires an energy-averaged LEED pattern. Nevertheless, the qualitative agreement between Figs. 3(a) and 3(b) is quite gratifying.

In order to more carefully study the transition between the rhombic and FCI surface structures, we monitored the intensities and widths of diffraction spots of the rhombic and rectangular patterns as a function of temperature while heating the sample at a rate of 0.1 K/sec. The results, shown in Fig. 5, indicate that there was a rather abrupt transition from the rhombic to rectangular pattern at around 800 K. This transition was irreversible based upon the observation that the data of Fig. 5 are unchanged (except for variations ascribable to Debye-Waller effects) when the data were acquired at $T \leq 120$ K after each annealing step, or were acquired at the annealing temperature directly. The width of the diffraction spots are close to the resolution limit of the LEED apparatus, and correspond to an effective domain size of, or greater than, 150 Å.

Our study indicates the existence of two distinct stages in the regrowth of the twofold surface of icosahedral

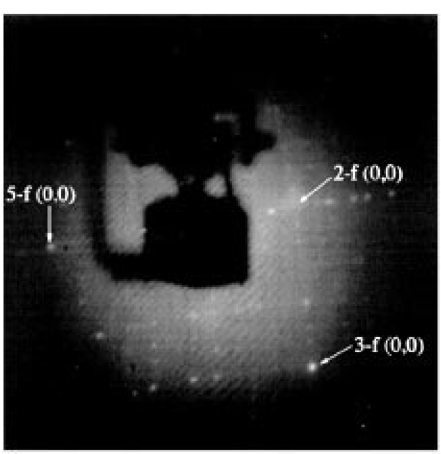

FIG. 4. LEED pattern taken at the periphery of the sample showing evidence of faceting. Arrows denote the (0, 0) beams for the twofold surface as well as the threefold and fivefold facet surfaces.

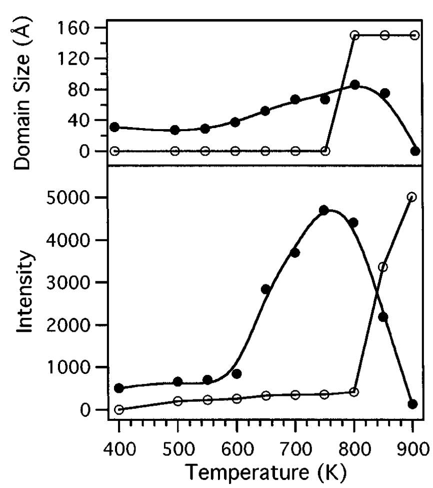

FIG. 5. Temperature dependence of the LEED intensities and domain size for the rhombic (solid circles) and rectangular (open circles) patterns. The lines serve as a guide to the eye. A distinct transition from the rhombic to rectangular pattern is observed at approximately 800 K.

Al-Pd-Mn that are correlated with the sample composition as well as the line shape of the Mn $2p_{3/2}$ peak measured by XPS. In the first stage, upon annealing the damaged surface between 600 and 700 K, a nanocrystalline (or nanoquasicrystalline) phase appeared. The rhombic LEED pattern associated with this phase, while very different from the expected FCI pattern, was orientationally coherent with the underlying bulk quasicrystal as well as the FCI LEED pattern that appeared at higher temperatures. The pattern itself consists of diffuse spots, precluding a definitive identification of this phase as quasicrystalline as opposed to, say, a rational approximant of the icosahedral phase [21]. Preliminary LEED measurements of the regrowth of the fivefold surface of icosahedral Al-Cu-Fe [22] indicate that this two-step regrowth process may be a general feature of quasicrystal surfaces.

At annealing temperatures above 800 K, a bulk-terminated FCI twofold surface was obtained, with evidence of faceting especially at the periphery of the sample. The composition of the surface, within statistical error, was the same as the bulk. Futhermore, the width of the Mn $2p_{3/2}$ XPS peak returned to the anomalously narrow value reported in previous XPS measurements of icosahedral Al-Pd-Mn. This point is significant since it is consistent with the prior suggestion that the line shape of the Mn $2p_{3/2}$ peak may be used as a fingerprint of the FCI phase within the Al-Pd-Mn family. Taken together, these results show that after a careful annealing cycle, high quality bulk-terminated twofold surfaces of icosahedral Al-Pd-Mn may be obtained. Further investigations of this surface by STM are planned to address directly the discrepancies observed in previous STM measurements of this material.

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