Surface Structural Transitions on the Icosahedral Quasicrystal $Al_{70}Pd_{20}Mn_{10}$

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We report the observation in real space of a structural transition on the surface of the quasicrystal $Al_{70}Pd_{20}Mn_{10}$ from icosahedral to body-centered cubic caused by bombardment with 1.5-keV Ar^+ ions. Subsequent annealing at 700 K restores the quasicrystalline structure of the surface. In addition to illustrating the sensitivity of the surface structure to local stoichiometry and demonstrating the thermodynamic stability of the quasicrystalline state, our observations open the way to investigating the assembly kinetics on quasicrystalline surfaces. [S0031-9007(98)06453-9]

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The surfaces of quasicrystals are of interest for a number of reasons. Quite apart from their extraordinary structure, which presents an immense challenge even for established methods such as low-energy electron diffraction [1], neutron and x-ray diffraction [2], and scanning tunneling microscopy [3,4], these surfaces have remarkable physical and chemical properties which suggest a number of technological applications [5,6]. Additionally, since the thermodynamic stability of quasicrystals is due not only to a particular crystallographic structure, but also to a stoichiometry that must be maintained within narrowly defined limits, quasicrystalline surfaces should be sensitive to variations in local composition [7].

In this Letter, we report real space observations, using secondary-electron imaging (SEI) [8,9] of a surface structural transition on the quasicrystal $Al_{70}Pd_{20}Mn_{10}$ from icosahedral to body-centered cubic (bcc) induced by bombardment with 1500-eV Ar^+ ions. Subsequent annealing at 700 K restores the icosahedral structure at the surface and this cycle can be repeated reproducibly. Although *bulk* phase transitions have been observed in quasicrystals which have been irradiated by high-energy ion or electron beams [10–14], our observation is the first of a structural transition at a quasicrystalline *surface*. This introduces several new factors compared to bulk transitions, such as the nature of the interface between the bcc and icosahedral structures and the type and extent of ordering at the surface. But, most important, because the SEI measurements were carried out *in situ*, our observations open the way to studying the assembly kinetics of icosahedral units on quasicrystalline surfaces.

SEI is a method for obtaining real-space information about the local geometric arrangement of atoms near a surface [9]. Direct projection imaging of the interatomic directions, produced by the forward-focusing effect in electron-atom scattering [15], is responsible for the formation of the pattern. Images can be recorded while the sample is rotated, which provides three-dimensional views of the structure. Thus, twofold, threefold, and fivefold symmetry axes in icosahedral $Al_{70}Pd_{20}Mn_{10}$ have been observed with equal precision and the angles between them found to be in agreement with icosahedral-point-group symmetry [8]. For a structural transition, as reported here, SEI allows the correspondence of the high-symmetry axes of these structures to be identified, from which the relative orientation of the initial and final structures can be readily determined.

The experiments were performed in an ultrahigh vacuum chamber with a total pressure in the lower 10^{-10}-Torr range. The pentagonal surface of a single-grain $Al_{70}Pd_{20}Mn_{10}$ quasicrystalline sample of size 8×4 mm^2 was oriented with the x-ray Laue method to within $\pm 0.25°$ and mechanically polished before insertion into vacuum. Polycrystalline samples of pure Al and Pd were used for calibrating x-ray photoelectron spectroscopy (XPS) data. XPS was used to determine the cleanliness of the surface of the sample and its chemical composition at different stages of treatment. Chemical information in XPS was obtained by measuring the intensity of photoemitted electrons that are element-specific. For our purposes, the ratio of the Pd $3d$ and Al $2p$ peak intensities was obtained for the quasicrystal and compared with that obtained in pure metals. The information depth in XPS, determined by the mean-free-path of photoelectrons excited by AlK_α radiation [16], is approximately 1–1.5 nm. The escape depth of electrons used to generate the SEI patterns may be slightly longer, but one can safely assume that the information obtained by both measurements originates from a surface region of approximately the same thickness.

Figure 1 shows a secondary-electron pattern obtained from the quasicrystalline $Al_{70}Pd_{20}Mn_{10}$ sample after O and C surface contaminations have been removed by sputtering with Ar^+ (1500 eV; 10^{-8} A mm^{-2}) for two hours and then annealed at 700 K for 90 min. XPS measurements showed that the surface had the nominal bulk composition to within the experimental uncertainty

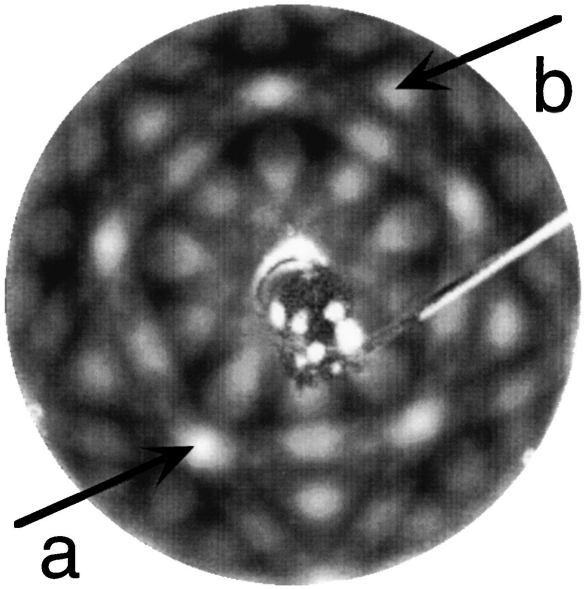

FIG. 1. Secondary-electron pattern obtained from a single $Al_{70}Pd_{20}Mn_{10}$ quasicrystal at a primary-electron energy of 2 keV. The center of the pattern is obscured by the shadow of the electron gun used for the excitation. The arrows point to a twofold- (a) and a threefold-symmetry (b) axis.

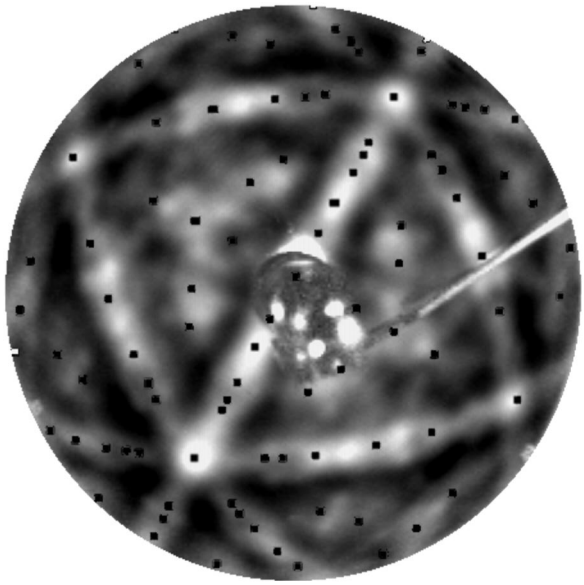

FIG. 2. Secondary-electron pattern from the quasicrystal in Fig. 1 after bombardment with Ar^+ ions, but before heat treatment. A central projection of directions in a bcc structure is superimposed on the pattern.

of $\pm 5\%$. The most striking feature in the pattern is the pentagonal symmetry. The five major bright patches that form the pentagon are distributed in azimuthal intervals of 72° on a polar circle with an opening (half) angle, θ, of 31.5° [17], as required by icosahedral symmetry. Each of these bright patches represents a twofold-symmetry axis, one of which is marked (a). This pentagon shares its twofold-symmetry axes with five other pentagons that are placed uniformly around its circumference, but are mostly outside the collector screen [8]. Adjacent to each side of the pentagon are bright patches arranged in five groups of equilateral triangles, the corners of which are the twofold axes. The centers of the triangles ($\theta = 38°$) represent five threefold-symmetry axes, one of which is labeled (b), but their apices ($\theta = 59°$) are outside the collector screen. These observations are consistent with the local icosahedral symmetry of the quasicrystalline surface [8,18]. Moreover, since SEI provides a probe for the crystallographic positions of the nearest local atoms around an average reference atom, the quality of the pattern in Fig. 1 leads to the conclusion that the analyzed portion of the sample has a high degree of orientational order.

Ion bombarding an alloy surface may result in modification of the surface structure and, more importantly, in the preferential removal of an alloy constituent. Thus, the chemical composition at the surface can be different from that of the bulk [19]. After sputtering with Ar^+, XPS showed that the composition of the quasicrystal surface is nearly $Al_{50}Pd_{50}$, with only trace amounts of Mn, i.e., there is a strong depletion of Al and Mn in the near-surface region. This freshly sputtered surface produces the secondary-electron pattern in Fig. 2. No features of pentagonal symmetry are discernible; instead, the pattern shows *orthogonal* symmetry. All the main features of this pattern can be accounted for by a direct projection of the vectors connecting the nearest-neighbor atoms with a reference atom for a bcc structure with the [110] direction oriented normal to the surface [20]. Such a projection is superimposed on the secondary electron pattern in Fig. 2. The agreement is excellent, apart from a few patches, probably generated by the wave nature of the electrons [15], which has been neglected in this (purely geometric) calculation. The most prominent features in this pattern are the two bright patches representing the $[11\bar{1}]$ and [111] directions, which lie approximately 70° apart at the top right and bottom left of the pattern, and the bright band, representing the (110) plane, which connects them. This plane is a mirror-symmetry plane for the [010] (left) and [100] (right) directions, which are separated by 90° [17]. Thus, while SEI demonstrates the existence of short-range order on the surface, the absence of a sharp low-energy electron diffraction pattern indicates that there is no long-range order.

Remarkably, beneath the few layers imaged by SEI, reflection Laue x-ray diffraction indicates that the icosahedral structure remains intact. This means that after ion bombardment the specimen is a bulk icosahedral quasicrystal covered with a layer of bcc units which have the same orientation as that used to generate the SEI pattern shown in Fig. 2. The lower bound for the thickness of the bcc layer corresponds to the information depth of SEI, which is approximately 2 nm [16].

The effect of annealing the ion-bombarded surface at 700 K is shown by the sequence of secondary-electron patterns in Fig. 3. The pattern in Fig. 3(a) was taken after the original surface (Fig. 2) was annealed for 15–20 min. Each successive pattern was obtained after annealing for additional 2-min increments. The differences between successive patterns are seen to be quite small, with the pattern in Fig. 3(c) showing the first discernible appearance of a pentagon. The quality of the image in Fig. 3(f) is not markedly different from that in Fig. 1 and additional annealing up to 45 min leads only to small changes resulting from the gradual reduction in the intensity of the original (orthogonal) pattern in Fig. 2. Upon completion of annealing, XPS shows that the chemical composition at the surface is restored to that of the bulk, a result of Al and Mn diffusion from the bulk to the surface during the annealing.

The contrast quality of the pattern in Fig. 2 confirms the long-range orientational order of the bcc units. Since our XPS measurements indicate that this surface has a chemical composition close to $Al_{50}Pd_{50}$, it is possible that the sputtered surface consists of the ordered AlPd phase in the $B2$ structure [21]. Thus, this high-temperature bulk β phase, which is not stable in the bulk at room temperature [22], could exist at the surface as a metastable structure.

A comparison of the high-symmetry directions in the $B2$ and the quasicrystalline structures obtained from Fig. 3 identifies their relative orientation, with the result shown in Fig. 4. The fivefold-symmetric quasicrystalline surface is depicted using the coordinates determined by Gierer *et al.* [1]. The interatomic distance is 2.964 Å, which is slightly larger than $a_R/\tau = 2.82$ Å, obtained from the quasilattice constant of $a_R = 4.562$ Å [2] with $\tau = (1 + \sqrt{5})/2$. Superimposed onto this network are several units of the $B2$ structure oriented with the [110] axis along the surface normal (the pentagonal axis). Here, the interatomic distance along $[00\bar{1}]$ corresponds to the Al-Al bond length of 3.05 Å and that along $[\bar{1}1\bar{1}]$ to the Al-Pd bond length of 2.64 Å [22]. Along the $[00\bar{1}]$ direction, the height of the pentagons is $(3/4 + \tau)^{1/2} \times 2.964$ Å $= 4.561$ Å, which should be compared with 1.5×3.05 Å $= 4.575$ Å, the length of 1.5 lattice constants of the $B2$ structure along this direction. Thus, along the $[00\bar{1}]$ direction, the mismatch between the β and the quasicrystalline lattice is only 0.3%. This results in an interface of these two phases which has

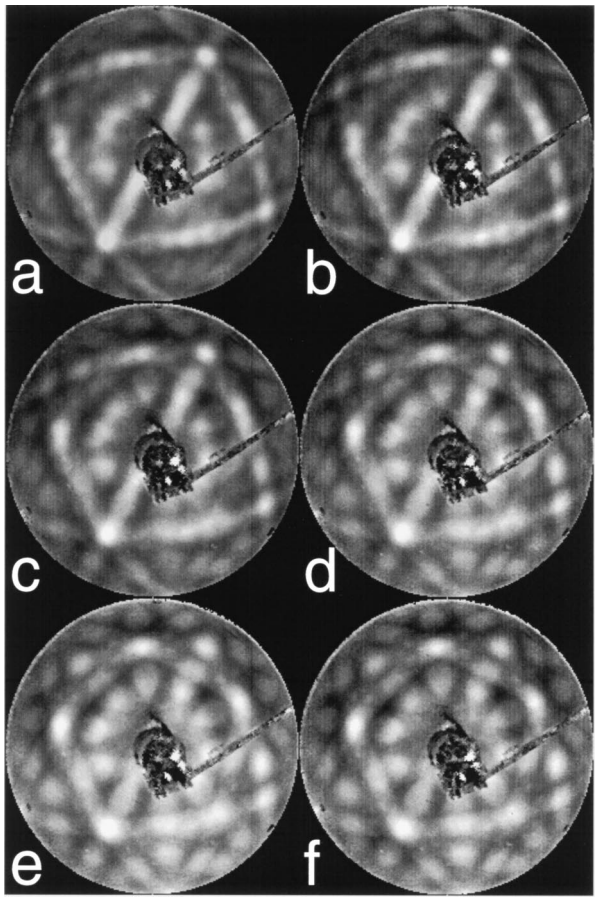

FIG. 3. Secondary-electron patterns of the ion-bombarded surface (Fig. 2) during annealing at 700 K. The image in (a) was taken after 15–20 min of annealing and the images in (b)–(f) taken at subsequent 2-min intervals.

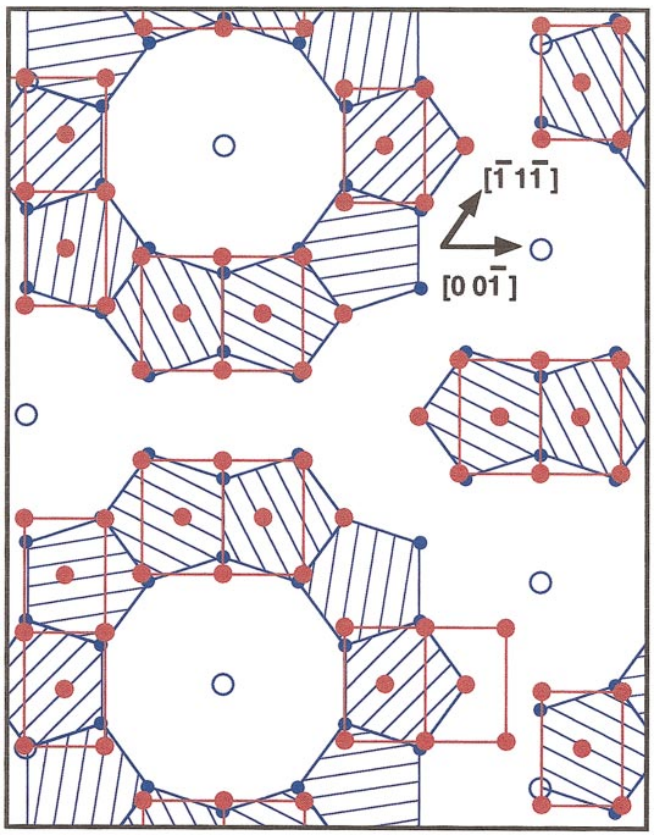

FIG. 4(color). An atomic model of the interface between the pentagonal surface of the icosahedral quasicrystal $Al_{70}Pd_{20}Mn_{10}$ (blue filled circles and hatched pentagons) and the (110) surface of bcc structural units (red filled circles). The interatomic distances are drawn to scale.

a high degree of structural registry and could explain the stabilization of the high-temperature β phase of AlPd near the surface [23].

The structural models of $Al_{70}Pd_{20}Mn_{10}$ in Refs. [1,2] both have the icosahedral symmetry required by this quasicrystal. Yet, they cannot reproduce the secondary-electron pattern in Fig. 1 with the same integrity as that generated from a pseudo-Mackay cluster, which consists of an inner dodecahedron with a central atom, an icosahedron, and an outer icosidodecahedron [24]. But this cluster is centrosymmetric and so does not have a preferred direction that causes the cubic structure to lock to one particular alignment. This can be reconciled only by the presence of some remaining structural defects when the $B2$ phase is annealed. These defects can be so minute as to be undetectable by SEI, yet sufficiently effective to align the cubic units at the surface. This highlights the fact that although the quasicrystal is the thermodynamically stable state, the relaxation to this state is quite sensitive to the history of the sample, particularly given the intermediate nonequilibrium bcc state produced by ion bombardment. Moreover, the available values for the diffusion constants of Mn and Pd in AlPdMn quasicrystals [25] follow an Arrhenius form over an extended temperature range and produce average diffusion lengths per unit time of $\dot{\ell}_{\mathrm{Mn}} = 1$ nm/s and $\dot{\ell}_{\mathrm{Pd}} = 7$ nm/s. Thus, it appears that the assembly kinetics of the quasicrystalline surface are diffusion limited. But considerable additional work will be required to identify the atomistic kinetic mechanisms responsible for the most remarkable of our observations, namely, the long-range orientational coherence across the entire macroscopic surface of both the bcc and annealed quasicrystalline structures.

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