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Formation of a well ordered ultrathin aluminum oxide film on icosahedral AlPdMn quasicrystal

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We have exposed the pentagonal surface of icosahedral AlPdMn quasicrystal kept at 700 K to several hundred langmuirs of O_2, which results in the formation of a 5 Å thick, well ordered aluminum oxide film. The local structure of the film resembles that of the oxide layers formed on ordered binary alloys of Al except that the quasicrystalline substrate makes the film consist of five pairs of nanometer-size aluminum oxide domains exposing their nominal (111) faces parallel to the substrate surface and rotated by 72° with respect to each other. The orientational relationship between these domains and the substrate is a consequence of the affinity of the icosahedral structure of AlPdMn to the CsCl structure.

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I. INTRODUCTION

Quasicrystals form a third state of atomic ordering besides the periodic and amorphous structures. They exhibit sharp electron- and x-ray-diffraction patterns characteristic of long-range orientational, such as five-, eight-, or tenfold, and quasiperiodic translational order.[1] Crystal-quasicrystal interfaces are of special interest due to the several unexpected phenomena that occur at the conjunction of different but nevertheless related structural properties. After preparation methods of well-defined quasicrystalline surfaces have been established, a great amount of different materials has been deposited on quasicrystalline substrates.[2] Besides pseudomorphic growth and heterogeneous nucleation, the growth of self-size-selecting crystalline domains in the nanometer range has been observed. In the case of Co deposition, for instance, five CsCl-type 20 Å large CoAl domains exposing their (110) faces parallel to the pentagonal surface of the icosahedral (*i*-)AlPdMn quasicrystal, rotated by 72° with respect to each other, are formed.[3]

Crystal-quasicrystal interfaces can also be generated by means of sputtering of quasicrystalline substrates. An ion-bombardment-induced modification of the stoichiometry in a near-surface region destabilizes the quasicrystal structure. In case of *i*-AlPdMn, sputtering of the fivefold-symmetry surface with Ar^+ leads to the formation of CsCl-type AlPd domains. Two possible orientations of the crystalline domains, depending on the sputtering conditions (temperature, angle of incidence, and predeposits), are generated. Domains are observed which expose their (110) as well as (113) faces parallel to the pentagonal surface. Additionally, both single-domain overlayers as well as overlayers consisting of five domains rotated by 72° with respect to each other are found.[3]

The above examples of crystal-quasicrystal interfaces demonstrate that there is a close relationship between the *i*-AlPdMn structure and the CsCl structure. The orientation of the sputter-induced CsCl-type domains on *i*-quasicrystals was explained by Steurer by the optimum matching of the average structures.[4] Similarly, body-centered-cubic (bcc) Fe, bcc Ni, bcc Co, and CsCl-type CoAl domains are found on the pentagonal surface of *i*-AlPdMn.[5]

Metal oxide interfaces are of considerable interest since they are, among other applications, important supports for dispersed metal catalysts and magnetoelectronic devices.[6,7] The oxidation of aluminum single crystals leads to the formation of thin amorphous oxide layers.[8] On the contrary, after oxidation at high temperatures, surfaces of alloys such as NiAl, Ni_3Al, CoAl, or FeAl consist of well ordered aluminum oxide films.[7] Especially, those films grown on Ni-Al alloys exhibit a high degree of crystallinity and a very low surface roughness and offer excellent reproducibility in preparation.[9] Consequently, oxides on Ni-Al crystal surfaces were chosen as a model for the selective oxidation of intermetallic alloys. NiAl possesses the CsCl structure with a lattice constant of ~2.89 Å. We emphasize that sputter-induced AlPd domains have a lattice constant of ~2.88 Å. Oxygen exposure of the NiAl(110) face at high temperature leads to the formation of a well ordered oxide film, which possesses a crystal structure comparable to γ-Al_2O_3,[9,10] one of the transition phases of alumina used as a support in technical catalysis. The oxide overlayer was found to be 5 Å thick, if the substrate surface is exposed to oxygen until saturation, and oxygen terminated.[11] The unit cell of the terminating oxygen layer of the modified γ phase has $a_1 = 10.6$ Å, $a_2 = 17.9$ Å, and $\alpha = 88.7°$ as lattice parameters. The film has its nominal, since slightly distorted, (111) plane parallel to the NiAl(110) substrate surface and consists of domains with two possible azimuthal orientations determined by the alignment of the elementary oxygen cells along the $[1\bar{1}\bar{1}]$ and $[1\bar{1}1]$ directions of NiAl(110). The angle between the $[1\bar{1}0]$ direction of NiAl and both the $[01\bar{1}]$ and $[10\bar{1}]$ directions of the oxide domains is ±24°.[12] A structural refinement, using x-ray diffraction, has confirmed the structural models of the oxide layer.[11] Only recently, the stoichiometry and atomic positions in the oxide film have been determined using scanning tunneling microscopy and computations based on density functional theory.[13]

Chang *et al.* and Popović *et al.* have reported the oxidation of the fivefold-symmetry surface of *i*-AlPdMn for substrate temperatures between 105 and 870 K.[14,15] X-ray photoelectron spectroscopy (XPS) investigations on the oxide layers have shown that only the Al atoms of the quasicrystal bind to the oxygen, while Pd and Mn remain inert.[16] The formation of amorphous alumina layers for different oxidation conditions, such as oxygen partial pressure, exposure time, and substrate temperature, has been monitored by means of low-energy electron diffraction (LEED).

Here, we report the formation of a well ordered aluminum oxide film on the pentagonal surface of *i*-AlPdMn by exposure to O_2 at 700 K. The film consists of five pairs of domains similar to those of the γ-Al_2O_3 phase aligning their nominal (111) faces parallel to the substrate surface.[9] Each pair of domains is azimuthally oriented along one of the five twofold-symmetry axes lying on the pentagonal surface of the quasicrystal. The orientation of the domains with respect to the substrate is a consequence of the close relationship between the icosahedral structure of AlPdMn and the CsCl structure.

II. EXPERIMENT

An *i*-quasicrystal with a nominal bulk composition of $Al_{70}Pd_{20}Mn_{10}$ and grown by the Bridgman technique was oriented by the x-ray Laue method along a fivefold-symmetry axis and cut by spark erosion perpendicular to this direction.[17] The sample with dimensions of $7\times4\times1$ mm^3 was mounted on a goniometer and introduced into an ultrahigh vacuum chamber with a base pressure in the lower 10^{-10} mbar range. The sample temperature was measured with a chromel-alumel (*K*-type) thermocouple pressed onto the front surface, and the sample was heated from the backside using a resistance heater. A clean quasicrystalline surface was established by cycles of Ar^+-ion sputtering at 1.5 keV (10^{-7} A/mm^2) and annealing at 700 K. LEED and secondary-electron imaging (SEI) were used to investigate the structural order in a near-surface region and XPS to probe its chemical composition. The results are consistent with those previously reported,[18] so we assume that our preparation procedure leads to a bulk-terminated surface. A three-grid back-view display system, with a total opening angle of 100° and operated with a beam current in the low microampere range, was used for the LEED experiment. Patterns were recorded using a 16 bit charge-coupled device camera and were subsequently normalized by the overall response function of the display system in order to eliminate spurious signals. The photoionization of the sample was performed by a nonmonochromatized Mg K_α source, and the XPS spectra were recorded by a cylindrical mirror energy analyzer equipped with a postmonochromator. The total energy resolution was 1 eV.

During the adsorption steps, the oxygen (with a purity of 99.998%) partial pressure was maintained between 5×10^{-7} and 1×10^{-8} mbar, and the sample was kept at constant temperature and, after the evacuation of the oxygen out of the chamber, annealed at 700 K. Typical exposure times were 20 min for low adsorption, 4 h for high adsorption, and the annealing process was performed for 2 h. The exposure is given in langmuir (L) units ($1\text{ L}=1.3\times10^{-6}$ mbar s).

III. RESULTS AND DISCUSSION

A. Clean pentagonal surface

Figure 1(a) shows the LEED pattern of the pentagonal surface of *i*-AlPdMn obtained after cycles of Ar^+ sputtering and annealing at 700 K. The quality of the pattern indicates a well-established quasicrystalline order at the surface.[19] Five twofold-symmetry axes lying on the pentagonal surface are superimposed. These axes are parallel to the $[1\bar{1}0]$ directions of AlPd(110) domains which are obtained by sputtering of the pentagonal surface. No traces of crystalline AlPd domains present at the surface, generated by sputtering, could be observed by means of LEED and SEI after annealing.

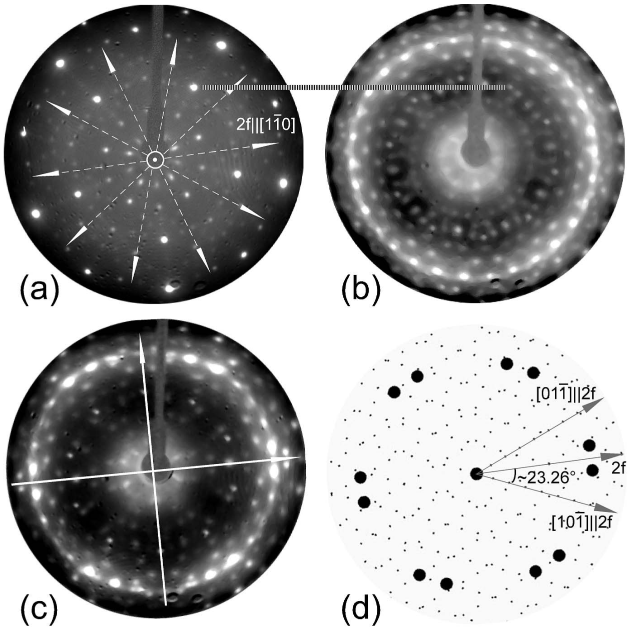

FIG. 1. LEED patterns obtained at a primary-electron energy of 55 eV from (a) the clean pentagonal surface of *i*-AlPdMn, (b) after exposure to 800 L O_2 at 700 K and subsequent annealing for 2 h, and (c) after Ar^+ sputtering the sample corresponding to (b) for 1 min and subsequent oxidation at 700 K. The weighted reciprocal lattice of one pair of ℓ domains is presented in (d) and oriented in accordance with the LEED patterns.

B. Oxidation of the pentagonal surface at high temperature

The LEED pattern displayed in Fig. 1(b) was recorded after exposing a freshly prepared quasicrystalline surface to 800 L O_2 at 700 K and subsequent annealing at the same temperature for 2 h. Ten peaks originating from the quasicrystalline substrate are still observable (emphasized by the dashed line). The presence of these spots suggests that despite the formation of an oxide overlayer, the quasicrystalline order is conserved by the segregation of Al atoms toward the surface.[20] It also indicates that the thickness of the film is comparable to that reported on NiAl which is 5 Å.[9] In the diffraction pattern, 30 very bright spots are located on a circle. Actually, all the spots originating from the oxide film form concentric elements of 30, 20, or 10 spots. A comparable density of reflections in LEED patterns was already observed for films generated by the oxidation of intermetallic alloys such as NiAl at a high substrate temperature.[11] The rotational symmetry of the pattern is consistent with the existence of multiple domains with different but well-defined azimuthal orientations. Spot-profile analysis suggests an average domain diameter of ~35 Å. Diffraction spots characteristic of the oxide layer, albeit inferior in quality, already emerge after a brief exposure of the clean surface to O_2 at elevated temperatures without postannealing. The presence of only one (00) reflection excludes a faceted structure of the growing film.

A multidomain structure is confirmed by the LEED pattern presented in Fig. 1(c), which was recorded after a brief ion sputtering, at an angle of 50° off the normal, of the surface, giving rise to the pattern presented in Fig. 1(b) and re-exposure to 300 L O_2 at 700 K and subsequent annealing. By this treatment, one azimuthal orientation of the domains is preferentially selected, because 12 of the 30 bright spots observed in pattern (b) are considerably brighter in pattern (c) compared to the remaining 18. The pattern is twofold symmetric and shows close similarities to that obtained after the oxidation of a NiAl(110) surface.[21] One of the two twofold directions of the structure, indicated in Fig. 1(c), is aligned with one of the twofold directions of the substrate.

We have applied this sputtering procedure to identify one of the five domains. Indeed, one orientation preferentially survives sputtering better than others. After sputtering, the sample is well annealed at the standard temperature of preparation, and LEED spots characteristic of the quasicrystal surface are discernible through the oxide layer. The pattern shown in Fig. 1(b) is a superposition of five patterns displayed in Fig. 1(c), each rotated by $2\pi/5$ relative to each other. We bare in mind that this process is useful only because it helps identify the domain structure of the oxide layer by singling out one domain. Note further that patterns similar to Fig. 1(b) have been observed for annealing and oxidation temperatures between 700 and 840 K. Such patterns have routinely been obtained for annealing times of about 1 h. No further improvement in the contrast quality has been observed for longer exposure and/or annealing times.

In order to confirm the oxidation of the Al atoms of *i*-AlPdMn only, XPS measurements were performed. In Fig. 2, the spectra of Al 2*p* states for the clean surface and after exposure to O_2 are displayed. Changes in the core levels of Mn and Pd could not be detected, as previously reported by Chang *et al.*[16] This confirms that the features observed in the LEED pattern after O_2 exposure of the quasicrystal arise from an aluminum oxide film. Within our limited resolution, we are not able to distinguish the occurrence of Al ions in two or more different oxidation states or coordinations.

C. Structure model

Structure models for the growing oxide film have been proposed in the case of the oxidation of the NiAl(110) surface at high temperatures.[11,13,22] Basically, it consists of two (111) γ domains in-plane oriented by ordering of the elementary oxygen cells along the $[1\bar{1}\bar{1}]$ and $[1\bar{1}1]$ directions of the NiAl substrate.[10] As displayed in Fig. 1 of Ref. 22, the two alumina domains each have an azimuthal separation angle of 24° with respect to the $[1\bar{1}0]$ direction of the intermetallic alloy and a total separation angle of 48° with respect to each other. The in-plane separation angle between the oxide domains is the same in all proposed structure models. Differences appear in the exact atomic positions inside these cells. Since the oxide layer may not necessarily have the Al_2O_3 stoichiometry and is, additionally, too thin for a unit cell be defined, and grossly strained and distorted,[13] we designate each cell of this structure the ℓ–phase and use it to represent the oxide layer on the quasicrystal surface.

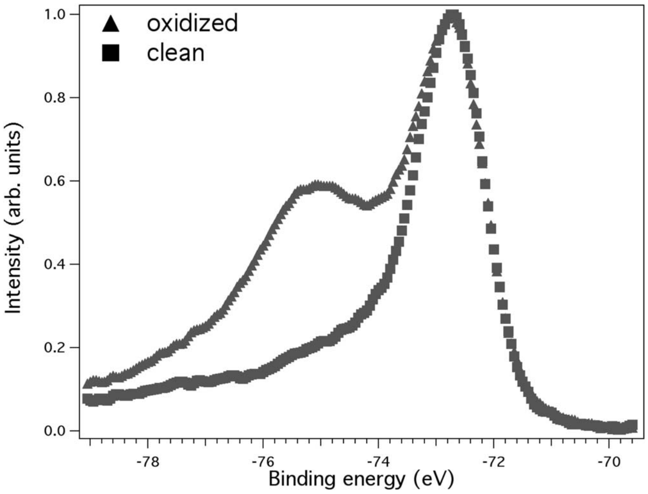

FIG. 2. XPS spectra of Al 2*p* core electrons from the clean surface (squares), responsible for the LEED pattern shown in Fig. 1(a), and after its exposure to 800 L O_2 (triangles), corresponding to the LEED pattern presented in Fig. 1(b).

Figure 1(d) displays the weighted reciprocal lattices of two (111) ℓ domains azimuthally separated by 46.5°. Weighted means that the structure factors are taken into account in the reciprocal-lattice calculation, i.e., spots which appear larger in the simulated pattern will appear brighter in the diffraction pattern.[23] The orientation and scale of the calculated pattern are chosen to match those of the diffraction experiments. All the diffraction spots arising from the alumina film present in Fig. 1(c) can be found in the simulated pattern. Unlike the NiAl case, the two ℓ domains are not separated by 48° but by 46.5° with respect to each other. This difference can be accounted for by the 0.74° angle mismatch between the $[1\bar{1}\bar{1}]$ and $[1\bar{1}1]$ directions of the CsCl structure and the in-plane twofold-symmetry axes of the i-structure, as shown in Fig. 3. In fact, the pentagonal surface of *i*-AlPdMn is closely related to (110) surfaces of CsCl-type structures with a lattice constant of about 2.9 Å, while an in-plane twofold-symmetry axis corresponds to the $[1\bar{1}0]$ direction.[3] Therefore, an orientation of the ℓ domains determined by the in-plane twofold-symmetry axes, and hence similar to the orientation on NiAl(110), is reasonable. However, this fundamental orientation relationship is slightly modified since atomic rows in the oxide layer (in the $[10\bar{1}]$ and $[01\bar{1}]$ directions, see Fig. 3) align with twofold-symmetry axes rather than the $[1\bar{1}\bar{1}]$ and $[1\bar{1}1]$ directions of the CsCl structure. Consequently, two ℓ domains are rotated by $48° - 2 \times 0.74° \simeq 46.5°$ with respect to each other. The bright spots present in Fig. 1(c) correspond to a lattice parameter of

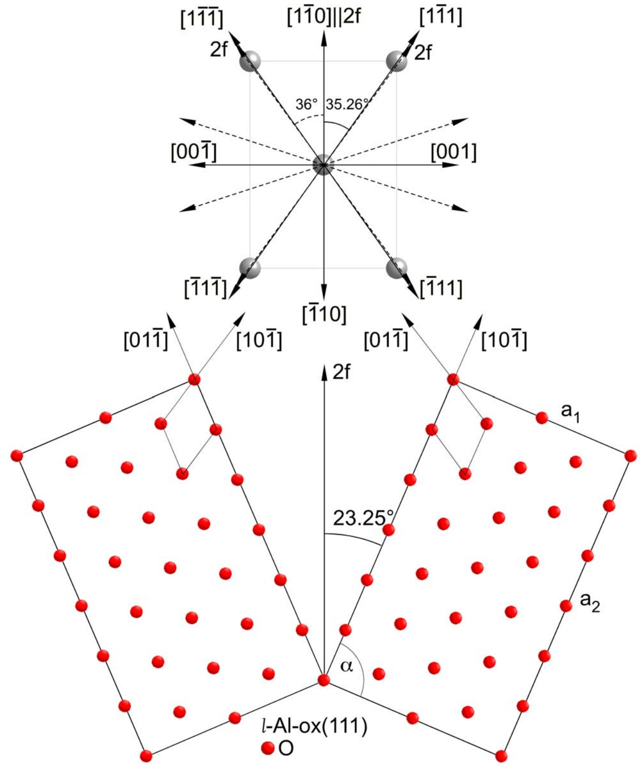

FIG. 3. (Color online) (top) Orientational relationship between the pentagonal surface, represented by the in-plane twofold-symmetry axes (dashed arrows), and the closely related (110) surface of a CsCl-type structure (spheres, solid arrows). (Bottom) A possible orientation between a pair of ℓ domains and the fivefold-symmetry surface of *i*-AlPdMn, represented by an in-plane twofold-symmetry axis. The unit cell of the oxide layer is represented by the lattice parameters a_1, a_2, and α. Elementary oxygen cells are symbolized by rhombohedra.

2.59±0.02 Å, which is close to the distance of 2.60 Å between two rows of O atoms in the oxide structure.[9] This argument is based on the average quasicrystalline structure deduced from its long-range properties. An atomistic interface model based on the local arrangement of atoms would therefore not be reliable for the present case and not be compatible with the quasicrystalline order at the surface.

The agreement of the pattern displayed in Fig. 1(d) with the pattern in Fig. 1(c) confirms that the oxide film consists of five pairs of ℓ domains. The pairs are rotated by 72° with respect to each other. All diffraction spots observable in pattern Fig. 1(b) can be accounted for by this structure model. It is consistent with the fact that no preferential twofold-symmetry axis exists at the quasicrystalline surface, i.e., each of the five twofold-symmetry directions present at the fivefold-symmetry surface of *i*-AlPdMn should equally promote the alignment of a pair of ℓ domains. The formation of a well ordered alumina film on the pentagonal surface of *i*-AlCuFe quasicrystal was previously reported.[24] However, in this case, only one azimuthal orientation of the aluminum oxide domains was observed, unexpected from a quasicrystalline material in the icosahedral structure presenting seeds with multiple degrees of freedom for the alignment of a growing layer. In the light of our observations that one of the five domains can be promoted by Ar^+ bombardment, it is conceivable that the *i*-AlCuFe samples were mechanically manipulated in one direction prior to oxidation and/or there exists a preferential growth direction in the multidomain quasicrystalline structure which gives rise to the growth of the oxide material in one direction.

IV. CONCLUSION

We have observed the formation of crystalline domains on the pentagonal surface of *i*-AlPdMn after exposure to oxygen at a substrate temperature of 700 K. Five pairs of ℓ domains exposing their (111) faces parallel to the surface and rotated by 72° with respect to each other are formed. The orientational relationship between these domains and the substrate is a result of the close relationship between the icosahedral structure of AlPdMn and the CsCl structure. The principal difference of the present observation from oxide layers on ordered binary alloys is the self-size-selecting and self-assembling nature of the domains on the quasicrystalline substrate.

During oxidation, strong Al-O bonds are formed in favor of Al bonds in the quasicrystal alloy. Al segregation from the bulk to the surface promoted by the elevated temperature re-establishes the chemical conditions at the Pd site for quasicrystalline alloying by supplying the missing aluminum atoms to Pd. We therefore believe that the formation of the oxide layer also involves Pd atoms in a near-surface region of the quasicrystal. Hence, the conditions for growing an ordered surface oxide layer may critically depend on the local conditions, e.g., Al-to-Pd concentration ratio at the surface, oxygen partial pressure, and temperature. In the previous work, these conditions for crystalline growth may apparently not have been satisfied.[14,15]

By virtue of the relative ease of preparation of the oxide film in the form of nanometric domains, quasicrystals bare the potential use of catalyst carriers of active metals without resorting to self-size-selecting processes of growing films. The natural limit of the lateral size may promote them to attractive substrates for nanoscale epitaxy. Furthermore, the chemically inert oxide layer acts as an efficient capping on the quasicrystal surface and may lead to technological applications of quasicrystals.

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