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Surface structures of cleaved icosahedral Al-Pd-Mn single quasicrystals after heat treatment

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Surfaces produced by *in situ* cleavage fracture in ultrahigh vacuum of Czochralski-grown icosahedral Al-Pd-Mn single quasicrystals were investigated by scanning tunneling microscopy and by scanning electron microscopy at ambient temperature and after heat treatments of up to 670 °C. It is found that the evolution of the surface structure with temperature depends very sensitively on the local stoichiometry. In areas of suitable composition a cluster-subcluster structure similar to that observed at room temperature is maintained whereas in areas of slightly different composition a terrace structure atomically flat over relatively large areas develops. The results are discussed in the general framework provided by current models of quasicrystal formation. [S0163-1829(98)06605-3]

I. INTRODUCTION

The structure of icosahedral Al-Pd-Mn quasicrystal surfaces has been the subject of a number of recent investigations. Indeed, the surface properties of quasicrystals have attracted considerable attention after the discovery that, in addition to exceptional physisorption and chemisorption properties, these materials exhibit low coefficients of sliding friction making them attractive for use as technical coatings.[1] Furthermore, studies of Al-Pd-Mn quasicrystal surfaces by scanning tunneling microscopy (STM) (Refs. 2 and 3) and by low-energy electron diffraction (LEED) (Refs. 4 and 5) have demonstrated that understanding the properties of quasicrystal surfaces poses an especially difficult problem. It is now generally accepted that the particular lattice symmetry, the stability, and the physical properties of quasicrystals are associated with a substructure consisting of large atom clusters.[6–9] Therefore, a quasicrystalline solid cannot retain its specific properties up to the very surface if the cluster substructure is not maintained there. In addition, quasicrystalline phases have the character of intermetallics owing their stability not only to a particular structure but also to the chemical order and the maintenance of very narrow limits with respect to stoichiometry. This should make quasicrystal surfaces particularly sensitive to changes in composition.

In this paper we report on the results of a study carried out by STM and by scanning electron microscopy (SEM) on clean Al-Pd-Mn quasicrystal surfaces obtained by cleavage fracture in ultrahigh vacuum (UHV). During heat treatments of up to 670 °C, we find that the evolution of the surface structure depends very sensitively on local stoichiometry. Differences in composition of the order of the measurement uncertainty of present analysis techniques are decisive for whether a cluster structure similar to that observed at room temperature is maintained or whether a structure consisting of atomically flat terraces develops.

II. EXPERIMENTAL

The samples with dimensions of $3\times3\times8$ mm^3 were cut by spark erosion from Czochralski-grown single quasicrystals about 7 cm in length and 7 mm in diameter. Their composition of $Al_{70.5}Pd_{21}Mn_{8.5}$ was measured by inductively-coupled plasma optical emission spectroscopy (ICPOES). After mechanical grinding and polishing, the samples were transferred to the UHV chamber [pressure $(0.5-2)\times10^{-8}$ Pa] of the scanning tunneling microscope and cleaved perpendicular to twofold and fivefold quasicrystal lattice directions by a double-wedge technique. They were transferred on to the scanning tunneling microscope without breaking the vacuum and inspected in the constant-current mode at room temperature. Subsequently the samples were heat treated in steps of 2.5 h at temperatures of up to 670 °C. For this treatment the samples were removed from the scanning tunneling microscope and, again without breaking the vacuum, transferred to an electron-beam heating device, where the beam was applied from the rear of the sample holder in order to avoid any risk of surface damage. The sample temperature was measured by a phosphorescence-based technique up to 400 °C and with a calibrated pyrometer at higher temperatures. After each heating step the sample was returned to the scanning tunneling microscope for investigation. Following the STM investigations the samples were studied by light-optical microscopy (LOM) and SEM in the secondary-electron imaging mode.

III. EXPERIMENTAL RESULTS

After cleavage at room temperature the Al-Pd-Mn quasicrystal surfaces exhibit (in LOM) a mirrorlike metallic optical reflectivity. In SEM no secondary phases can be recognized. However, a low density (between 5 and 50 mm^{-2}) of small voids of dodecahedral shape with a diameter between 5 and 40 μm can be seen. Cavities of this kind were first studied in Ref. 10 and have recently been investigated in detail by Auger spectroscopy in the same material as employed in the present work.[11] The results presented below were obtained in areas far away from the voids.

Figure 1 shows STM pictures obtained on twofold (a,b) and fivefold (c,d) cleavage planes at room temperature. The pictures taken at two different magnifications show a cluster-subcluster structure. The width of the smallest feature in (b) and (d) lies between 0.6 and 0.9 nm. We note that, due to the exponential depth dependence of the tunneling current, an

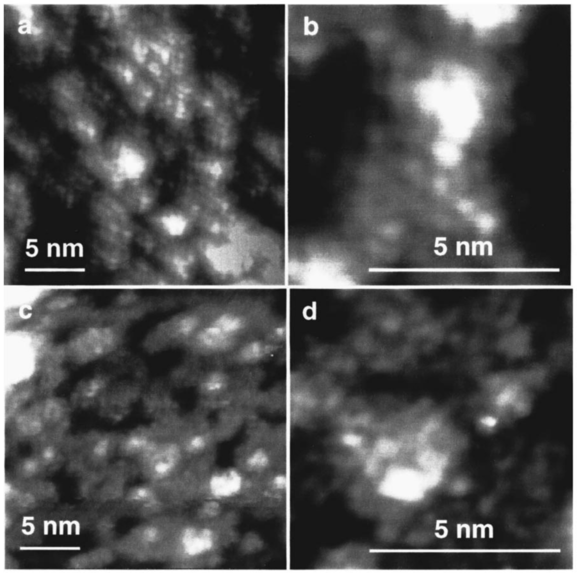

FIG. 1. STM images of the cleaved Al-Pd-Mn quasicrystal surfaces at room temperature. (a) and (b) show the cleavage surface perpendicular to a twofold direction at different magnifications, whereas (c) and (d) show the fivefold surface at two magnifications. The constant current images (1 nA current) were measured at tunneling voltages of -225, -300, -350, and -350 mV, respectively.

intuitive inspection of the contrast distribution leads to an overestimation of the depth dynamics. The actual maximum corrugation amplitude in (b) and (d) is only of the order of 1–2.5 nm. The absolute value of the tunneling currents is typically about 0.4–1 nA at a tip-to-sample voltage between 200 mV and 2 V. Figure 2 shows current-voltage characteristics at different fixed tip-to-sample distances. We recognize a metallic behavior without any indication of an irregularity in the electronic density of states.

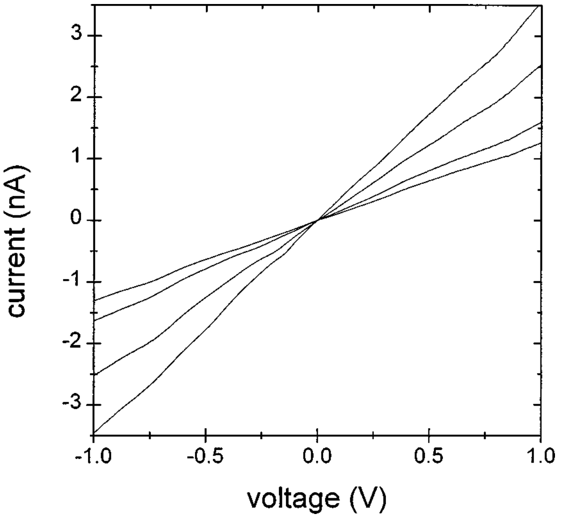

FIG. 2. Current-voltage characteristics of the twofold Al-Pd-Mn quasicrystal surface after cleavage at room temperature. The four sets of data correspond to four different tip-sample distances obtained by fixing different set currents at -250 mV tunneling voltage. Each data set consists of more than 1000 isolated current voltage curves.

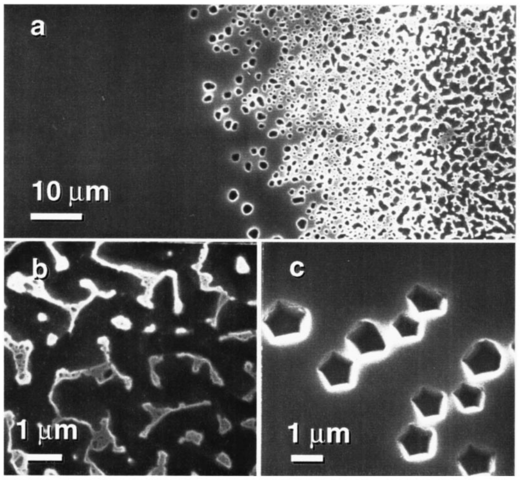

FIG. 3. (a) Scanning electron microscopy image of the cleaved and heat-treated fivefold icosahedral Al-Pd-Mn quasicrystal surface. In the left-hand part no modification occurred during heat treatment at 550 °C for 1 h, while in the right-hand part holes were formed by desorption. (b) Magnified area of a surface area with an almost full layer removed by desorption under the same conditions. (c) Faceted holes with a low density exhibiting a fivefold edge orientation.

We observed the cluster-based structure on all the samples investigated in this state, i.e., directly after cleavage, thus reproducing our earlier results.[3] Studying samples from five different quasicrystals taken from the top and the bottom part of the quasicrystal and taking pictures from a given sample from areas distributed over the whole cleavage surface we always observed a cluster-based structure.

When the samples are annealed above 420 °C the surface starts, in certain areas, to lose its metallic optical reflectivity and becomes matt, while in the other areas the metallic appearance is maintained. Figure 3 shows an SEM image of a partially modified fivefold surface heat treated at 550 °C. In the right-hand part of Fig. 3(a), the irregular contrast marks the areas appearing matt in the light microscope. On the left-hand side, the surface appears unchanged. This area corresponds to those parts of the surface exhibiting metallic optical reflectivity. On the right-hand side a high density of holes has formed. The matt appearance is the signature of these holes. With increasing time the hole concentration increases such that the holes overlap and almost a full surface layer is removed [Fig. 3(b)]. The hole formation rate is slow at 420 °C, but at 550 °C the surface structure changes within minutes. In areas where holes did not form at low temperature, no changes occur after further annealing at higher temperatures either. The holes are faceted and a fivefold edge orientation is clearly visible [Fig. 3(c)].

Figure 4 shows STM pictures of the morphology of fivefold planes in surface areas where the metallic reflectivity has been preserved. The pictures were recorded after heat treatment at 260 ± 5, 360 ± 5, 462 ± 5, and 566 ± 10 °C. The cluster-subcluster structure as such is unchanged. However, as shown in greater detail in Fig. 5, the cluster structure has become more regular and compared to the room-temperature result the images of the smallest clusters exhibit a slightly reduced size distribution, i.e., diameters in the range of 0.3–0.6 nm. A completely different surface structure exists in the

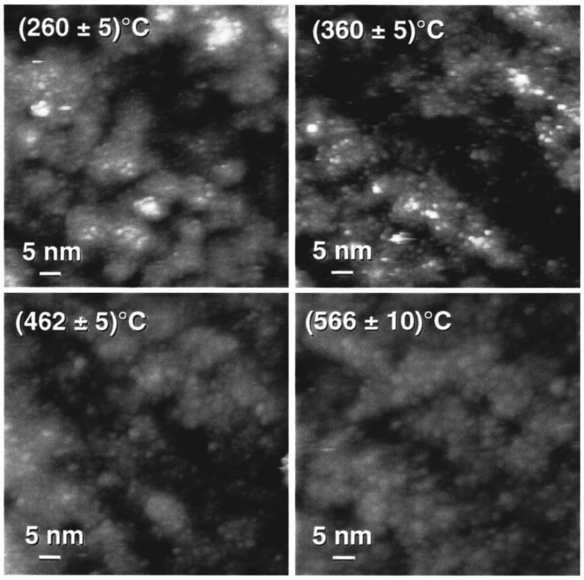

FIG. 4. Surface structure of the fivefold cleaved surface after heat treatment at (260±5), (360±5), (462±5), and (566 ±10) °C. The scan area is 70×70 nm^2. The images were measured at tunneling voltages of −1.5, −1.6, +1.6, and +1.7 V, respectively, (0.6 nA tunnel current). The corrugation is between 1.5 and 2.5 nm for all temperatures.

modified areas with matt appearance. Only here are flat terraces observed that are separated by steps (Fig. 6). Terraces with a lateral extension of up to 70 nm can be found. On these terraces the STM resolves a very irregular, nonperiodic structure giving rise to a very low corrugation, of the order of less than 0.1 nm, i.e., lower by more than one order of magnitude than the corrugation observed on the cluster-based structure.

IV. DISCUSSION

An interpretation of the STM contrast on the cleaved quasicrystal surfaces has already been given in Ref. 3. Only the essentials will be repeated here. The tunneling signal is the sum of all current contributions along the three-dimensional shape of the tip, weighted by the exponential dependence on distance. Therefore the possibility has to be considered that imaging artifacts arise either due to a simultaneous contribution of more than one tip area to the tunneling current or due to a possible convolution of the geometrical shapes of the scanned feature and of the tip. Indeed, we have occasionally observed such complex multiple-tip effects. Nevertheless we found that, under suitable conditions, pictures of the type shown in the previous section could be obtained in a stable and reproducible manner independent of the scanning direction and of the particular tip used.

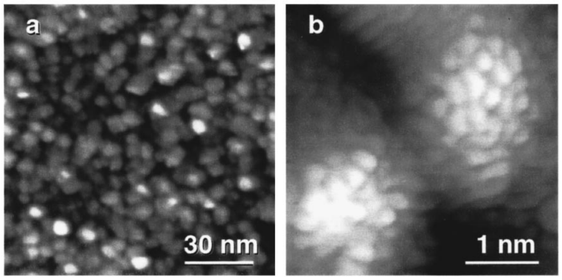

FIG. 5. (a) Cluster-based structure observed in a surface area maintaining its metallic reflectivity during annealing at (580 ±40) °C for 2.5 h. (b) High-resolution image of (a). (a) and (b) were measured at tunneling voltages of −1.1 and −0.67 V, respectively.

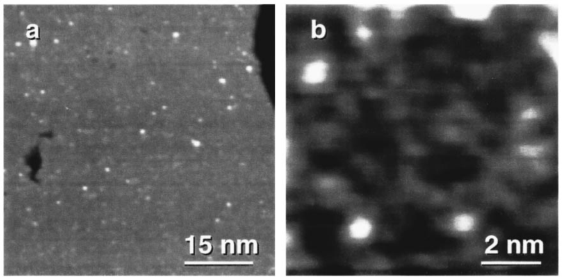

FIG. 6. (a) Flat terrace with a corrugation of less than 0.1 nm observed in an area affected by evaporation such as that in Fig. 3(b) during annealing at (550±10) °C for 2.5 h. (b) High-resolution image of the terrace structure [enhanced contrast compared to (a)]. The images were measured at a tunneling voltage of −1.5 V.

In the structural model of the icosahedral Al-Pd-Mn quasicrystal[9,12] the basic structural element is a cluster derived from the Mackay icosahedron.[13,14] It consists of three centrosymmetrical shells with a total number of 51 atoms and an overall diameter of 0.9 nm. The Mackay-type clusters form deep potential wells to which electrons are thought to be bound in almost ''magic'' numbers, similar to the case of isolated clusters, where particularly stable configurations are observed at special atom and electron numbers. This model is supported by theoretical calculations.[15] For these clusters no dangling-bond-type protrusions or a strong modulation of the electron density of states are expected. This explains the smooth and structureless density of states observed on the clusters.

Our tunneling spectroscopy data indicate a metallic behavior of the surface at room temperature. A metallic behavior has also been found by photoemission spectroscopy of an icosahedral $Al_{70}Pd_{20}Mn_{10}$ alloy.[16,17] Photoemission spectroscopy of the same material as studied here revealed a higher density of states at the Fermi energy at the surface compared to the bulk.[18] In Ref. 9 a hopping-type conductivity with a positive temperature coefficient is expected for the bulk, but deviations towards a metallic behavior are predicted close to defects or surfaces due to the break in symmetry there.

For a discussion of our results obtained during heat treatment we first address the question of the origin of the surface changes observed by SEM. Our investigations show that, at temperatures above 420 °C, significant amounts of material are removed from the surface by evaporation. Furthermore, faceted holes are formed at higher temperatures. For Al-Fe-Cu the formation of comparable faceted holes has been attributed to surface melting and sublimation.[19] Under our ultrahigh vacuum conditions a surface melting would automatically lead to desorption, as we conclude from the high vapor pressures of Al and Mn under Knudsen conditions. Desorption cannot be expected to be stoichiometric, because the vapor pressures of the three elements present in the quasicrystal differ considerably. In particular, the relatively low vapor pressure of Pd should lead to a relative enrichment of this element. Although the details of the desorption are not yet known, the modified areas show signs of restructuring towards a new steady-state structure. We use this expression here since under Langmuir conditions in UHV, where the material is not in equilibrium with its vapor pressure, the structure of the surface reached after prolonged heat treatment may differ considerably from its equilibrium structure.

We explain the observation that at temperatures up to 670 °C thermal desorption occurs only in specific areas but not in others on the basis of the assumption of a local composition variation. Unfortunately, our knowledge of the single-phase existence range of icosahedral Al-Pd-Mn is still very limited. According to the phase diagram of Gödecke and Lück[20] the existence range of the icosahedral phase in Al-Pd-Mn is very narrow. It is only about 3 at. % wide at 840 °C, where according to the very sparse data, the range adopts a maximum width. However, there is increasing evidence that the single-phase region is indeed much narrower. It is an empirical fact corroborated by an extended study in which samples of more than 20 single quasicrystals were analyzed by x-ray and electron microscopic techniques and by ICPOES that, in Czochralski growth, the highest quality single quasicrystals have a composition of $Al_{70.5}Pd_{21}Mn_{8.5}$ and that the stoichiometry has to be kept within limits of better than $\pm 0.5\%$.[21] We note that this is at the limit of the accuracy of the best ICPOES data and that it is at present not possible to achieve such an accuracy with any local-probe technique. In addition, it was found that millimeter-sized samples taken from different areas both in lateral and vertical cross sections all along high-quality Czochralski-grown single quasicrystals show composition variations in the order of $\pm 0.5\%$.

We therefore interpret Fig. 3 as the image of an area exhibiting a composition gradient from left to right of the order of magnitude discussed above. At temperatures of up to 670 °C the stoichiometry of the alloy on the left-hand side is such that it is essentially stable to thermal desorption. Since in STM this area shows the cluster structure, we conclude that this stoichiometry corresponds to some optimum value under which a cluster structure shows maximum stability. In contrast, on the right-hand side the stoichiometric conditions are such that desorption takes place. At present it is too early to say anything definite about the mechanism. However, the formation of extended terraces which, according to the STM pictures, are atomically flat may point to a surface melting process. We note that the most recent data on Pd- and Mn-tracer diffusion in Al-Pd-Mn yield diffusion coefficient of $D_{\mathrm{Pd}}(T) = 1.2\times 10^{-2}\times \exp(-2.31\ \mathrm{eV}/kT)\ \mathrm{m}^2\,\mathrm{s}^{-1}$ (Ref. 22) and $D_{\mathrm{Mn}}(T) = 8.9\times 10^{-4}\times \exp(-1.99\ \mathrm{eV}/kT)$ $\mathrm{m}^2\,\mathrm{s}^{-1}$,[23] respectively, ($k$ is the Boltzmann constant and T the absolute temperature). With the well known bulk-diffusion relation of $r = (6Dt)^{1/2}$ (t denotes the time) and the assumption of a correlations factor of 1 (since no data is available) the characteristic diffusion length per unit time (r/t) is at 500 °C 7 nm/s for Pd and 23 nm/s for Mn. This means that diffusive migration should be sufficiently fast for substantial mass transport at this and higher temperatures.

We conclude that desorption from quasicrystal surfaces and the accompanying structural modifications are highly sensitive to composition. This result is not really surprising taking into account the fact that, even in the bulk, the stability range of the icosahedral phase is very narrow. It further underlines the complexity of the task of preparing a surface of a quasicrystal with the aim of obtaining a structure as close as possible to that in equilibrium by applying conditions under which the system must necessarily evolve along trajectories far away from the equilibrium state. It is worth noting that even for simple binary intermetallic compounds the preparation of the equilibrium surface structure corresponding to a minimum of the Gibbs free energy of the system in equilibrium with its vapor phase is a formidable task.[24] The thermodynamically stable quasicrystalline phases known to date are all ternary or higher intermetallic compounds. Their behavior with respect to surface structure, composition, and treatment is further complicated by the importance of long-range atomic interactions, where a scale of some ten nanometers is connected with the cluster-subcluster structure.

We now briefly discuss earlier work on the production of surfaces of icosahedral Al-Pd-Mn. With the exception of Ref. 3 where the same cleavage technique was employed as in the present work, the clean surfaces could not be produced *in situ*. Therefore, the surfaces prepared in air were ion bombarded to remove the oxide layer after transfer of the samples into the ultrahigh vacuum. The ion bombardment changed the composition, due to the mass-dependent sputtering yield. In the work of Schaub and co-workers[2] the surface composition determined by x-ray photoelectron spectroscopy (XPS) changed from a nominal average composition of $Al_{68}Pd_{23}Mn_9$ to $Al_{59}Pd_{39}Mn_2$. By suitable annealing the Al and Mn depleted surface can be driven back closer toward its initial composition. In Ref. 2 a final composition of $Al_{68}Pd_{27}Mn_5$ was reached after annealing at 1050 K. In STM the surfaces thus prepared exhibited flat terraces containing holes and starlike spot patterns of fivefold symmetry. Gierer *et al.*[4] started with a nominal composition of $Al_{70}Pd_{21}Mn_9$ and reached a final composition of $Al_{70.5\pm0.8}Pd_{23.1\pm0.6}Mn_{6.4\pm1.2}$ determined by XPS.[25] These surfaces exhibited LEED patterns of fivefold symmetry. From the intensity and sharpness of the LEED spots the authors concluded that the surface is atomically flat and has a high structural quality. Shen *et al.*[5] investigated the regrowth path after sputtering and annealing treatments of Al-Pd-Mn in order to arrive at LEED patterns exhibiting quasicrystal symmetries. They found that a two-stage regrowth procedure was necessary to obtain an atomically flat surface with a composition of $Al_{73\pm2}Pd_{19\pm2}Mn_{7\pm2}$. All these contributions indicate that the occurrence of flat terraces is closely connected with significant regrowth procedures involving substantial composition changes.

From our discussion it is obvious that, at present, the surfaces obtained by cleavage fracture in the UHV are the only ones whose structure can be linked in a fairly direct way to that of the bulk. Indeed, this procedure avoids all the chemically disruptive steps of surface treatment inherent in the ion bombardment and annealing route. On the other hand, further work is required in order to clarify the extent to which the observed structure and properties are typical of the equilibrium surface. Although our present work has demonstrated that the cluster-subcluster structure represents the stable state up to 670 °C, we cannot at present show conclusively that structure and composition of the clusters observed after the heat treatment are still the same type of Mackay-type cluster observed at room temperature. This reservation is even more valid for the elements of the surface structure obtained by the sputter-and-annealing technique.[2,4,5] Finally, we note that the surfaces of the dodecagonal voids found in the Czochralski-grown single quasicrystals are probably the only equilibrium quasicrystal surfaces produced to date. These voids have grown inside, the volume under Knudsen conditions, i.e., in equilibrium with the material's vapor pressure. Analyzing the internal surfaces of these voids by local-probe Auger techniques after cleavage fracture of Czochralski-grown single quasicrystals, Suzuki and co-workers[11] found that, compared to the bulk, they were enriched in Pd and depleted by Mn.

V. CONCLUSIONS

Surfaces produced by *in situ* cleavage fracture of Czochralski-grown icosahedral Al-Pd-Mn single quasicrystals in ultrahigh vacuum were investigated by scanning tunneling microscopy and by scanning electron microscopy at ambient temperature and after heat treatments of up to 670 °C. It is found that the evolution of the surface structure with temperature depends very sensitively on differences of the local stoichiometry in the order of the measurement uncertainty of present analysis techniques. In areas of suitable composition a cluster-subcluster structure similar to that observed at room temperature is maintained, whereas in areas of slightly different composition a terrace structure atomically flat over relatively large areas develops during significant evaporation of material from the surface. The results are explained with the current models of quasicrystal formation and stability based on highly stable clusters.

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