Irreversible Structural Transformation of five fold i-AlPdMn Quasicrystals after Ion Bombardment and Annealing

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ABSTRACT

Five fold i-AlPdMn surface prepared under UHV by ion bombardment and annealing was so far considered to be bulk terminated. This result was substantially based on a quantitative LEED analyses [1]. Analysis of the specular rod in a X ray diffraction experiment at grazing incidence supported this result [2]. We present a new study of this surface by high resolution X ray diffraction at normal incidence. In this Bragg configuration the diffraction peak 18 – 29 for instance is at a photon energy of 2.873keV, the 72 – 116 reflection at 5.725keV. This results in an analyzed thickness of the sample surface of a few micrometers.

The surface was cleaned by ion bombardment. During annealing (T≅880K), we clearly observed the progressive disappearance of the initial Bragg peak characteristic of the as cast bulk sample. Conversely a new Bragg peak grows at an energy position shifted by 1eV compared to the position of the original Bragg peak. This is a clear signature for an irreversible structural transformation which takes place on at least the micron thickness. On the transformed surface, both, a LEED pattern and a RHEED pattern, characteristic for a five fold surface were easily obtained.

This high resolution experiment (the relative Bragg peak shift is $3 \cdot 10^{-4}$) was reproduced on samples from different initial compositions. This shows that five fold i-AlPdMn surface changes after preparation by ion bombardment and annealing at 900K on a micrometer thickness. This is not consistent with the conclusion that the surface is simply terminated by a cut of the original bulk. We conclude that a reorganization process of the quasicrystalline structure during annealing proceeds in the surface vicinity (probed depth is close to a few microns).

INTRODUCTION

Thanks to the possibility to produce icosahedral AlPdMn quasicrystal single grains at the cm scale with an almost perfect long range order [3-7] and short range order [8] this compound serves today also in surface science as a model system. Because of its chemical reactivity however, AlPdMn surfaces cannot be studied adequately in air where an aluminum oxide layer covers the whole sample surface [9] but requires a surface preparation under UHV (Ultra High Vacuum). Two different possible requirements on a clean surface intrinsic to the quasicrystal can be desirable: firstly a thermodynamic equilibrium between surface and the volume and secondly

a simple cut of a perfect structure [10]. These demands led in the past to the use of essentially two distinct surface preparation methods under UHV on the five fold i-AlPdMn surface. Ebert et al. have developed fracture of the AlPdMn quasicrystal as a surface preparation technique in order to preserve chemical composition and atomic order at the surface [11]. The resulting rough surface at the nm scale was then analyzed to be determined by the cluster elements emerging of bulk models. When annealing a fractured sample a high sensitivity to the starting composition has been observed [12]. A second surface preparation method consists in sputtering and annealing of a previously oriented and polished sample. This preparation technique was widely studied by different groups [13-16]. The sputter process cleans the surface from any contaminant but leaves an amorphous and chemically perturbed surface [16]. The following annealing processes is supposed to reorganize the sample surface with the hypothesis that the bulk acts as an infinite atom reservoir. Detailed studies reveal a division in at least three different annealing temperature regimes. A quasicrystalline surface characterized for instance by a sharp five fold LEED (Low Energy Electron Diffraction) pattern can then be stabilized for annealing temperatures between 700K and 1000K [16]. In this annealing temperature range the bulk composition is restored at the surface or nearly so [14,16]. A further strong fingerprint for this quasicrystalline surface is the Mn $2p_{3/2}$ line shape observed in XPS (X ray Photoelectron Spectroscopy) [14,16]. Lower and higher annealing temperatures lead both to a crystalline surface structure with a strongly different chemical composition compared to the nominal bulk composition [14,16]. For higher temperatures the crystalline surface thickness depends directly on the annealing time, as a preferential manganese evaporation seems to be at the origin of the structural change [16].

In this article we intend to focus on the quasicrystalline surface.

Up to now this surface is commonly accepted to be simply terminated by the bulk. This is essentially based on a quantitative LEED analyses [1] but also analysis of the specular rod in a X ray diffraction experiment at grazing incidence [2] and more recently low energy ion scattering measurements [17] at the surface supported this result. Scanning Tunneling Microscopy (STM) revealed, that this surface preparation led to flat terraces with step height sequences compatible with the Fibonacci chain [18-20]. The step heights could directly be identified as distances between dense atomic planes in established bulk models. Recently STM images with atomic resolution have been obtained on these flat terraces. The observed atom positions are consistent with existing bulk models [21]. However these results where obtained only after at least one high temperature (T > 850K) annealing, whereas already annealing temperatures between 700K and 850K exhibit high quality 5 fold LEED pattern but with a rough surface morphology at the nm scale [5,22-24]. This result is also consistent with results presented by C. Jenks which also show that annealing temperatures of about 900K are required to obtain flat terraces at the micron scale without large clusters still observed at lower temperatures [14].

We want to underline, that both surface preparation methods (fracturing and sputter/annealing) lead to significantly different surface morphologies which were however both analyzed to be bulk terminated.

EXPERIMENTAL DETAILS

In this article we will show two main evolutions of the sample observed after surface preparation by sputtering and annealing. We therefore examined the samples using different Synchrotron X ray techniques. All presented measurements were performed on the ID 32 surface science beam line at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). In a first part we show X ray experiments giving supplementary information concerning the yet mentioned morphology change from a rough to a flat surface when annealing temperature achieves 900K. In the second part X ray diffraction experiments in normal incidence geometry show that at the same temperature a structural change in a several micron thick region is observed.

The incident beam energy was scanned using a standard Si (111) channel cut monochromator leading to an intrinsic energy resolution of about $\frac{\Delta E}{E} \approx 10^{-4}$. A grazing incidence geometry was used for the X ray reflectivity measurements and X ray surface diffraction experiments. The reflectivity is recorded in vicinity of the total reflectivity angle which is at about 0.24° in the case of AlPdMn [5]. In the case of X ray surface diffraction rod scans perpendicular to the surface are scanned. As this technique is not a surface sensitive technique, these scans are largely influenced by the bulk signal. Surface signal can yet be observed between the bulk diffraction peaks. In the case of quasicrystals with their dense reciprocal space however further experimental analysis is required. Comparison between spectra obtained on the prepared surface and spectra collected on a sputtered surface allow to distinguish bulk signal and surface diffraction signal without any doubt. These experiments were performed on a Bridgmann grown single grain with a nominal composition of $Al_{72}Pd_{19.5}Mn_{8.5}$ (Ames Lab, T.A. Lograsso, D. Delaney).

Secondly, the X ray Diffraction experiments in normal incidence geometry were performed on four different samples. In all cases the grain size was typically several millimeters. We studied a Bridgman grown single grain of nominal composition close to $Al_{72}Pd_{19.5}Mn_{8.5}$ (sample A) prepared by Ames Lab (T.A. Lograsso, D. Delaney). We used further three Czochralski grown samples with nominal compositions of about $Al_{70.4}Pd_{21}Mn_{8.6}$ (sample B, Y. Calvayrac) and $Al_{68.2}Pd_{22.8}Mn_9$ (sample C and fractured sample, M. Boudard/M. de Boissieu). Sample A, B and C were all cut and mechanically polished in order to obtain a five fold axis perpendicular to the surface. In contrary the in air fractured specimen served as a reference sample as it showed almost perfect dynamical behavior [7]. For purposes of maximizing the intrinsic energy width of the rocking curve compared to the mosaic spread caused by strain, we studied the diffraction peaks at almost normal incidence ($\Theta_B > 88°$). This corresponds for instance to an incident photon energy of about 2.87keV for the 18-29 and of about 5.725keV for the 72-116 Bragg reflection leading to a probed specimen surface thickness contributing to Bragg reflection of about 2 μm and 10 μm respectively. The diffracted beam passed a voltage biased plate. The drain current to neutralize this plate is then proportional to the reflectivity. During annealing the specimen temperature was determined from the peak energy shift due to thermal sample expansion, which turned out to be much more accurate than the lecture of the mounted thermocouple.

Results

From the surface ...

In a first step we followed the evolution of the surface morphology by X ray reflectivity and X ray surface diffraction measurements while annealing temperature is increased [5, 22, 23]. For annealing temperatures below 900K no surface diffraction signal is observed which could indicate flat surfaces. For these low annealing temperatures annealed and sputtered surfaces led both to the same spectrum. Moreover, the observed reflectivity curve on the annealed surface is clearly not consistent with a flat surface, but must be analyzed with a surface region of diminished electronic density. This can be either explained with a modified chemical composition at the surface and more precisely with an increased aluminum concentration either with a short scale surface roughness. A changed chemical composition is definitely not consistent with our XPS measurements so that we clearly favor surface roughness in order to explain the observed reflectivity curve. This is fully consistent with the above mentioned experimental results obtained by STM. We want to underline that reflectivity curve and surface diffraction signal did not evolve with extended annealing time at the same annealing temperature well below 900K. For higher annealing temperatures (T ≥ 900K) however both, surface diffraction spectra and reflectivity, suddenly change and are now clearly consistent with large and flat surfaces in the micron scale defined by the transversal coherence length [5, 22, 23].

... to the bulk

Secondly we followed systematically the Bragg peak evolution for different samples during strictly tracked surface preparation cycles. Measured FWHM (full width at half maximum) of the Bragg reflections have to be compared to reflections obtained on the fractured reference sample, which turned out to show almost perfect dynamical behavior characterized by X ray Standing Wave technique [7]. Figure 1 shows the high agreement between this measured and the calculated 18-29 reflectivity. The calculation is based on dynamical theory. The relative FWHM is close to $1{,}5 \cdot 10^{-4}$. For a correct analysis the intrinsic experimental broadening induced by the Si (111) monochromator had to be taken into account. Beyond, this reference specimen is a "brother" to sample C coming from the same growth.
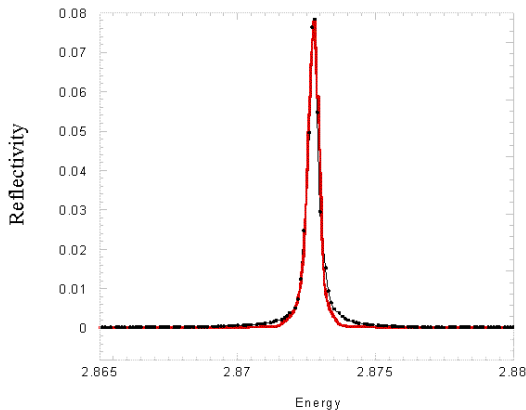

Figure 1: Almost perfect 18-29 Bragg reflection measured on a fractured Al-Pd-Mn sample (spotted line) . Thick line is the calculated reflection based on dynamical theory in a perfect quasicrystal.
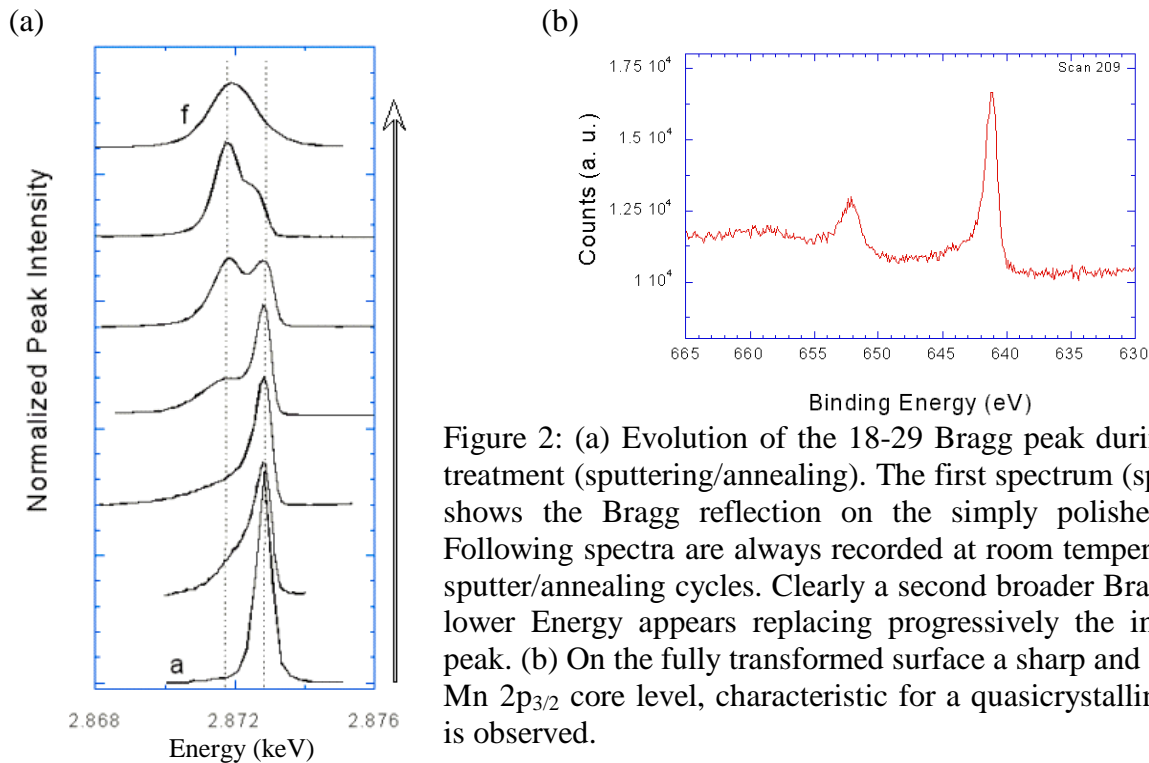
(a)

(b)

Figure 2: (a) Evolution of the 18-29 Bragg peak during surface treatment (sputtering/annealing). The first spectrum (spectrum a) shows the Bragg reflection on the simply polished sample. Following spectra are always recorded at room temperature after sputter/annealing cycles. Clearly a second broader Bragg peak at lower Energy appears replacing progressively the initial Bulk peak. (b) On the fully transformed surface a sharp and symmetric Mn $2p_{3/2}$ core level, characteristic for a quasicrystalline surface, is observed.

Figure 2 shows the evolution of the 18-29 Bragg peak on sample A as observed during several surface preparation cycles. The first spectrum (a) is taken on the polished sample surface, whereas the other spectra are taken at room temperature between subsequent sputter/annealing (T≅880K) cycles. At this annealing temperatures however preferential evaporation phenomena can still be neglected and 5 fold surface is commonly observed after the annealing process [16]. The progressive disappearance of the initial Bragg peak characteristic of the as cast bulk sample during the experiment is manifest. Conversely a new Bragg peak grows at an energy position shifted by 1eV compared to the position of the original bulk diffraction peak. The total annealing time to induce the complete change is of some hours. This observation is a clear signature for a structural transformation which takes place on at least the whole probed thickness of about 2 μm. However we observed on the transformed surface very sharp Mn $2p_{3/2}$ line shape (figure 2 (b)), which is a strong signature of the quasicrystalline surface [14,16]. This line shape is very sensitive to surface structure and its narrowness is suggested to serve as a signature of the bulk-like surface and to indicate the sample quality [14].

We observed a similar structure modification on sample B. This time we followed the 18-29 reflection during one long time annealing cycle. Figure 3 shows four spectra. Spectra a and b are taken within some minutes after 2 hours total annealing time, whereas Spectra c and d are taken 2 hours later. The peak splitting is again observed. On the transformed surface we observed afterwards easily an electron diffraction pattern (figure 3 (b)) with five fold symmetry characteristic for a quasicrystalline surface.
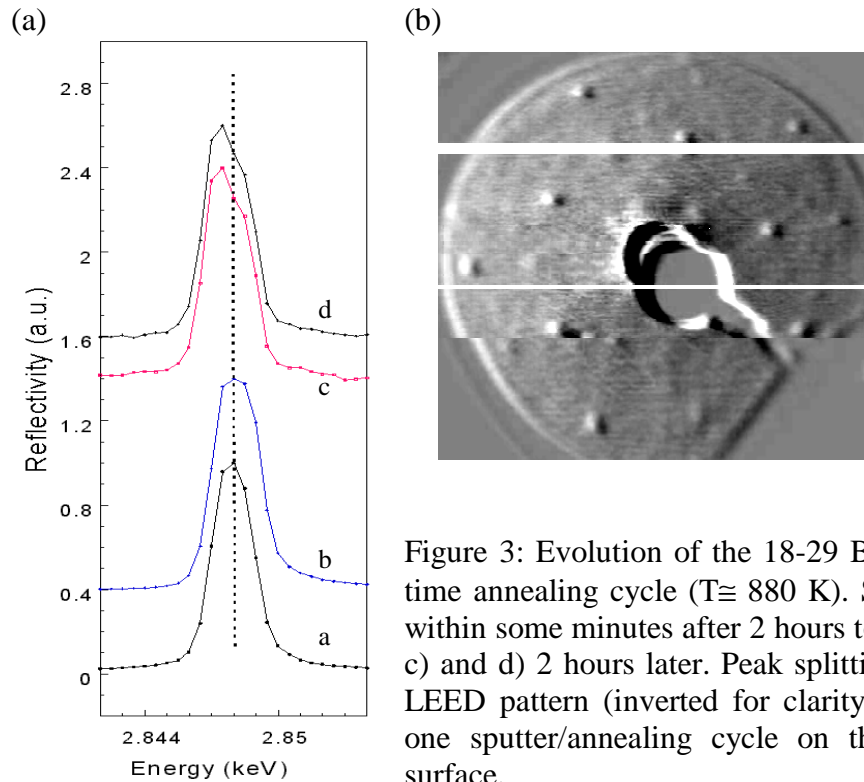
(a)

(b)

Figure 3: Evolution of the 18-29 Bragg peak during one long time annealing cycle (T≅ 880 K). Spectra a) and b) are taken within some minutes after 2 hours total annealing time. Spectra c) and d) 2 hours later. Peak splitting is clearly observed. The LEED pattern (inverted for clarity) was easily obtained after one sputter/annealing cycle on the completely transformed surface.

As last example we present the 72-116 Bragg peak evolution on the polished sample C. This time annealing cycles at about (T ≅880 K) without sputtering was performed (figure 4). This annealing temperature is just high enough to induce spontaneous de-oxidation at the surface [16]. The spectra, showing again a peak splitting for this different Bragg reflection, are all taken at room temperature between the annealing cycles. In consequence of the enhanced penetration length we see that the structural modification progress even to at least 10 μm below the surface. After the complete transformation a sharp electron diffraction pattern was again easily observed (figure 4 (b)). As this pattern was obtained in a second UHV chamber after an *in air passage* and in order to avoid sample melting by the always critical high temperature annealing, a clean surface was now prepared using ion sputtering (one sputter/annealing cycle was sufficient to obtain the presented LEED pattern). This however has no influence on the bulk part of transformed surface thickness.

We want to underline that after mechanical polishing the reflection widths on all samples are broader than on the fractured reference sample (cf. figure 1). However, due to a high quality polishing, sample A stands soonest a direct comparison. But within the observed surface transformation all specimen present much broader FWHM.
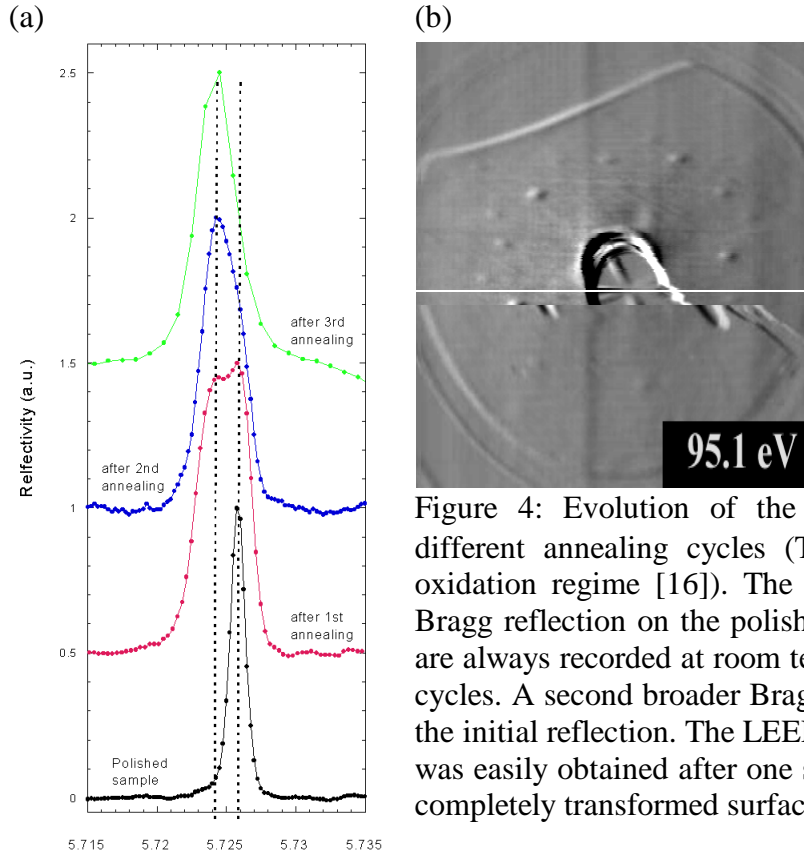
(a)

(b)

Figure 4: Evolution of the 72-116 Bragg peak during different annealing cycles (T≅ 880 K, spontaneous De-oxidation regime [16]). The first spectrum (a) shows the Bragg reflection on the polished sample. Following spectra are always recorded at room temperature between annealing cycles. A second broader Bragg peak replaces progressively the initial reflection. The LEED pattern (inverted for clarity) was easily obtained after one sputter/annealing cycle on the completely transformed surface.

Discussion and Conclusion

It must be pointed out again, that at a photon energy of about 3 keV the analyzed thickness of the sample surface is of few μm. This is obviously not the same sampled thickness of the aforementioned surface studies where only some nm are involved (LEED, XPS, ...). However this high resolution experiment (the relative Bragg peak shift is $3 \cdot 10^{-4}$), reproduced on samples from different origins, shows that the five fold i-AlPdMn surface changes after preparation by ion sputtering and annealing on a μm thickness. This is of course not consistent with the
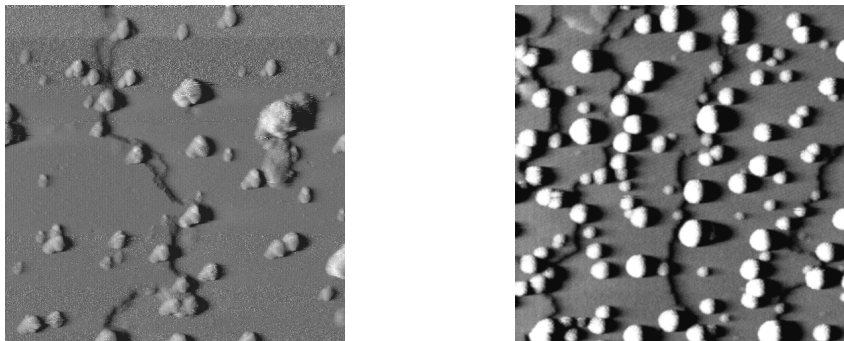

Figure 5: *In situ* Scanning tunneling microscopy (1250x1250Å^2) showing the progressive appearance of surface precipitation observed on sample A.

conclusion that the surface is simply terminated by a cut of the original bulk. It suggests more

likely, that a reorganization process of the quasicrystalline structure during annealing starts at the surface and progresses towards the volume.

All three samples differ quite remarkably in their original bulk composition. However after a high temperature surface preparation, on all three samples the aforementioned Bragg peak transformation has been observed. An identical five fold LEED pattern in terms of peak position and symmetries however has been observed after the full transformation. As this structure change is also observed on the only annealed sample C, we believe that annealing is the driving force of this structural change.

To complete our vision we have also performed *ex situ* SEM (Scanning Electron Microscopy) and *ex situ* AFM (Atomic Force Microscopy) studies on the fully transformed surface. This is necessary to identify possible phase separations which occur on some samples after annealing treatments. Here the results differ clearly between the different samples. On sample A, *in situ* STM experiments pointed out clearly the progressive appearance of many precipitates (figure 5). Further sputtering and annealing could only increase this tendency up to a wide surface covering by the precipitates as identified also by SEM (figure 6 a). This severe island precipitation at the micron scale with a chemical composition of about Al_3Mn determined by SEM (X ray fluorescence) is also easily visible by *ex situ* AFM [5]. In contrast a careful analysis of samples B and C by SEM and by AFM shows no clear evidence for surface precipitation. Nowhere on the surface chemical variations could be identified, SEM only indicates arose porosity (figure 6b). Porosity of the same type has also been observed by Ebert et al. after heat treatment at about the same temperature on cleaved samples [12]. This porosity is a distinctive behavior of these surfaces. It may be related to bulk holes and vacancy precipitation from the bulk. AFM show the creations of flat parallel terraces at the micron scale (figure 7). These terraces produce certainly the observed LEED pattern which are observed after the irreversible surface transformation. We want to underline that the mediocre quality of the observed LEED pattern on sample B and C is mainly due to firstly a rather poor initial polishing of the both samples and secondly that the LEED pattern have been observed in a second chamber
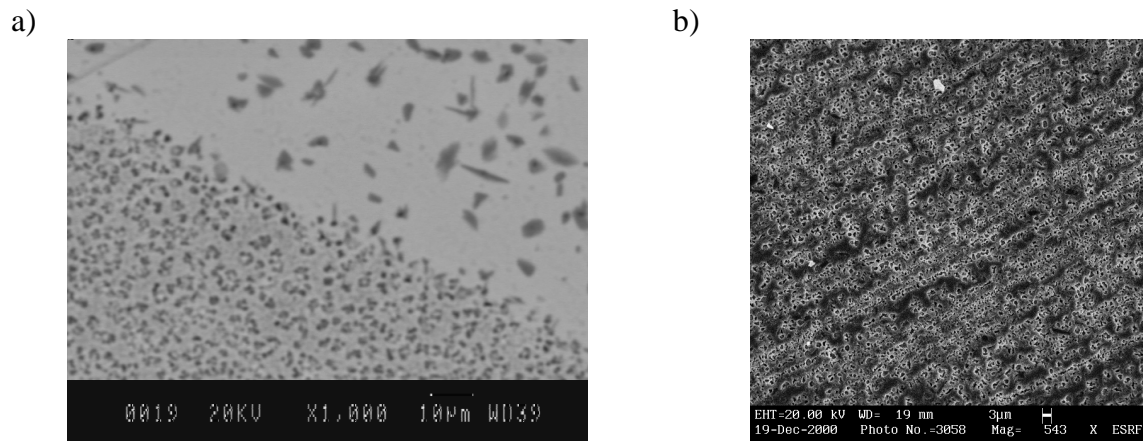
a)

b)

Figure 6: Scanning electron microscopy images of the sputtered/annealed fivefold Al-Pd-Mn quasicrystal surface after complete surface transformation. a) On sample A precipitation with chemical composition of about Al_3Mn are clearly observed on the right above part. b) On sample C a rough surface with no chemical precipitation is observed. This porosity is also observed on sample B.

and no effort in vacuum conditions (2·10^{-9} torr) and in sputter/annealing (only 2 sputter/annealing cycles after introducing of the samples) has been done to improve the diffraction pattern. On sample B, for instance, after careful re-polishing and only one sputter/annealing (T≅900K) treatment qualitatively high LEED pattern have been observed. In any case, second phases as they are observed on sample A are not detected here. Therefore this irreversible transformation cannot be directly related to some simple decomposition of an unstable sample.

The observed irreversible transformation leads to a surface showing quasicrystalline behavior in terms of electron diffraction which is however clearly not terminated by the original bulk. We observe this systematic irreversible Bragg peak transformation associated with no detectable surface precipitation or important surface precipitation. When it appears, the surface precipitation seems to be associated with the transformation process.

Our present scenario to gather all these observations is suggested by the high reproducibility and high stability of the observed LEED pattern which seems not to depend upon the details of the preparation. It seems that during annealing the surface evolves toward a composition and an atomic structure which is the best termination at the solid/vacuum interface. Surprising results are that the final surface is very close to the one deduced from the bulk structure and that the irreversible transformation is not a surface reconstruction but an irreversible transformation which involves at least a few microns below the surface. This interpretation is consistent with the occurrence of second phase precipitation in some samples which are initially too far from this locked quasicrystalline surface. It does not contradict the previous conclusions [1,2,17], that the surface is bulk terminated: i) the irreversible transformation is a small effect with a relative peak shift of 3·10^{-4}, ii) the surface is simply not the strict termination of the original bulk.
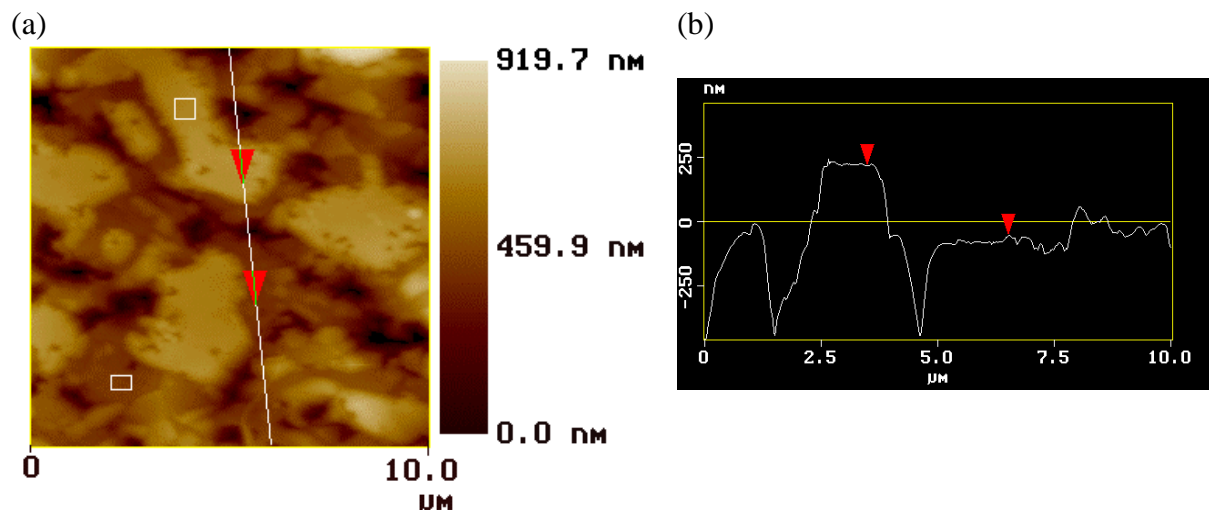

Figure 7: (a) Contact mode Atomic Force Microscopy image (height contrast) on fully transformed surface (sample C). Parallel flat terraces of micrometer scale are observed : surface normals of the two rectangles are parallel within about 0.8°. (b) Height signal along the indicated scan line.

Summary

The reproducible result is that an irreversible transformation of the quasicrystal is induced on the sputtered sample when it is annealed at temperatures close to 600°C (850K-900K). Strong indications of the so called bulk terminated surface (LEED, Mn $2p_{3/2}$ line shape) are however observed after the complete transformation. This coincides with a change in surface morphology of both sputtered [5,21-23] and cleaved samples [12], and with the fact that the exact starting composition is a critical parameter [12].

The presented new results do not contradict previous results (STM, LEED, XPD,...) but show that when probed at high resolution, the irreversible transformation of a thick layer below the surface (several micrometers) does not strictly support the idea that the surface is the termination of the unaffected bulk. To the contrary, the bulk seems to adapt itself to the surface preparation. This might carefully be considered for further studies as e.g. for homo-epitaxial growth studies.

Acknowledgement

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