Impurity phases in icosahedral Ag-In-Yb quasicrystal: influence in surface structure

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Abstract. We present scanning tunnelling microscopy (STM) studies of the fivefold surface of icosahedral (i) Ag-In-Yb quasicrystals grown under different conditions. The sample grown at a slower rate is found to exhibit impurity phases on the surface, whereas a faster growth rate yields a sample with a structurally perfect surface.

1. Introduction

Recent success in growing single grain samples of the icosahedral (i) Ag-In-Yb quasicrystal has opened up an opportunity to extend ultra high vacuum (UHV) surface studies beyond Al-based quasicrystals. These quasicrystals are isostructural to the binary i-Cd-Yb quasicrystal. The i-Cd-Yb quasicrystal is not suitable for surface studies under UHV because Cd evaporates upon heat treatments due to its high vapour pressure. Therefore, Cd is replaced by equal percentages of Ag and In that fulfils the Hume-Rothery criteria of the valence electron to atom ratio, e/a = 2.0 [1, 2].

We recently reported scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) studies of the fivefold surface of i-Ag₁₄₂In₁₄₂Yb₁₆ that show a step-terrace structure with quasicrystalline long range order [3, 4]. By comparing the terrace structure and step height distribution with the bulk structure model of i-Cd-Yb, it was found that the terraces are formed at bulk planes intersecting the centre of the rhombic triacontahedral clusters, the building blocks of the system [5]. However, due to the unavailability of the bulk model structure of i-Ag-In-Yb, it has not been possible to determine the exact distribution of Ag and In atoms.

Here, we report extended studies of the i-Ag₁₄₂In₁₄₂Yb₁₆ quasicrystal. We studied surfaces of two samples synthesized with different growth rates [2, 6]. One sample (hereafter referred to as Sample 1) was grown with a rate of 0.2 mm h⁻¹ [2], while another (Sample 2) was at 0.8 mm h⁻¹ [6]. Using scanning tunnelling microscopy, we identified phases with periodic structures on the surface of the sample grown at slower rate, whereas the other sample (grown at the faster rate) exhibited a comparatively higher degree of perfection.
2. Experiment
Both samples were grown using the Bridgman method. Details of growth conditions are reported in Refs [2, 6]. The orientation of the fivefold axis was determined using Laue backscattering. Laue patterns confirmed the fivefold diffraction from various areas of the sample [2]. The surfaces of both samples were prepared with the same process. Samples were cut perpendicular to the fivefold axis and polished down to 0.25 µm diamond paste. Subsequently, the surface was prepared in UHV chamber (base pressure 2 × 10⁻¹⁰ mbar by Ar⁺ sputtering (1-3 keV, 30-60 minutes) and annealing (at 715 K for 2-3 hours). The temperature was measured using an optical pyrometer with emissivity set at 0.35. An Omicron STM was employed to image the surface at room temperature.

3. Results and discussion
We first explain results from Sample 1 (the slower-grown sample). The surface was mirror-like after polishing. After annealing at about 400 °C, the sample develops different domains which were visible to the naked eye. Using a digital optical microscope, we observed at least six domains of various sizes within the sample area of 0.5 cm² (Figure 1). A homogenous contrast was observed in the optical microscope after the sample was gently polished. However, the domains routinely reappeared after annealing. This can be explained if atomic vacancies in the bulk diffuse to the surface during annealing and condense to form voids [7] affecting the reflectivity of the surface. The observation of different domains suggests a non-uniform distribution of voids in different domains. We investigated different fivefold samples cut from the same ingot. All sample yielded domains upon annealing.

We employed an electron probe micro-analyzer to determine the composition of four large domains. Two points were analyzed at each domain. The composition of the domains was found to be Ag₄₂In₄₂Yb₁₄.₉, Ag₄₁In₄₁.₇Yb₁₅.₂, Ag₄₁.₇In₄₃.₃Yb₁₄.₉ and Ag₄₁.₇In₄₃.₄Yb₁₄.₉. These values are close to the composition of the icosahedral phase. However, the grain boundary showed different compositions. The composition at the boundary of two randomly selected domains was Ag₄₀In₃₈.₂Yb₂₁.₈.

Although the domains had the same composition as the icosahedral phase, only two domains were found to yield quasicrystalline LEED patterns and STM images with the step-terrace structure expected from the bulk. The results presented in our previous publication were from one of these domains [3]. Another quasicrystalline domain is rotated slightly with respect to the primary quasicrystalline domain, resulting in a vicinal surface. Remaining domains were structurally poor to the degree that LEED patterns were very weak or absent. We identified local periodic structures on limited areas in these domains.

The vicinal domain was identified using LEED. The specular (reflected) beam from this domain was shifted from the specular position of the primary quasicrystalline domain. As expected for a vicinal surface, STM from this domain shows a high density of steps. Since the sample was polished uniformly using a rotating polishing pad, we rule out the possibility that the polishing treatment resulted in the vicinal surface. This is therefore likely to have originated during the sample growth or during post annealing treatments.

We identified various periodic structures in other domains. Figure 2(a,b) shows two different types of periodic structures imaged on the same domain. Periodic rows can be identified on the as-measured STM images (Figure 2 (a, b)). In order to extract further information, we analyzed Fourier transforms (FT), autocorrelation functions (AF) and Fourier pass filters (FF) of the STM images. The Fourier transforms (Figure 2 (e, f)) and the autocorrelation function (Figure 2 (c)) show sharp maxima revealing a periodic structure with excellent long range order within the experimental length scale. The autocorrelation function of the image reveals a rectangular unit cell of 2.14 nm × 3.08 nm size (Figure 2(c)). A slight distortion from a perfect rectangle is attributed to thermal drift present during the STM measurements. Using a Fourier pass-filter,
Figure 1. Ag-In-Yb sample demonstrating grain boundaries after annealing at 400 °C. Area of the sample is about 0.50 cm². The edge of the picture was removed to make a circular appearance.

Figure 2. (a, b) STM images taken from a domain showing two different periodic structures (a: 50 nm × 50 nm, b: 40 nm × 40 nm). (c) Autocorrelation function of image ‘a’. Inset: magnified image showing unit cell. (d) Image ‘b’ after Fourier pass-filtering. Inset: magnified image showing unit cell. (e-f) Fourier transform of images ‘a’ and ‘b’ respectively.

an oblique unit mesh (1.50 nm × 2.10 nm) has been measured on the STM image presented in Figure 2b. In addition to these periodic structures, we identified a periodic structure with an oblique unit cell (1.50 nm × 4.1 nm) on the terraces which were separated by steps of 1.7 nm. The step-height is related to the periodicity along the surface normal. We also observed weak LEED patterns from periodic domains. However, due to the low quality of the LEED patterns, it was not possible to extract the surface unit cell parameters accurately.

Occasionally, periodic microstructures are found to coexist with quasicrystalline structures. Example of such structures is given in Figure 3. These images were obtained from the primary quasicrystalline domain. Flat terraces are separated by steps of about 0.5 nm height. The Fourier
pass-filtering analysis reveals rectangular unit cells of 2.47 nm × 1.3 nm size on the terraces. This structure coexists with another periodic structure of oblique unit mesh with lattice parameters equal to 2.7 nm × 2.3 nm. A clear interface of these two structures is observed (Figure 3 (b)). The coexistence of different microstructures was observed also in Al-Pd-Mn grown by the self-flux method [8].

The observed periodicities do not seem to have a straightforward relationship with bulk terminations of the known phases of Ag-In-Yb. In the phase diagram of Ag-In-Yb, the 1/1 and 2/1 approximants are found in the vicinity of the icosahedral phase [2, 6]. They have cubic structures with lattice constant \( a = 1.57 \) nm and 2.53 nm, respectively. Other known phases are AgIn\(_2\) (tetragonal: \( a = 0.688 \) nm, \( c = 0.562 \) nm), In\(_4\)Ag\(_9\) (cubic: \( a = 0.992 \) nm), InAg\(_3\) (hexagonal: \( a = 0.295 \) nm, \( c = 0.786 \) nm), Ag\(_3\)In (hexagonal: \( a = 0.299 \) nm, \( c = 0.480 \) nm) and YbAg\(_{5.4}\)In\(_{6.6}\) (tetragonal: \( a = 0.973 \) nm, \( c = 0.571 \) nm) [9].

The observed step height of 0.50 nm is consistent with the periodicity along the [110] direction of the 1/1 approximant. The interplanar distance of a simple cubic lattice of lattice constant ‘a’ along the [110] direction is \( a/\sqrt{2} \). The step height of 0.50 nm is close to the half of \( a/\sqrt{2} = 0.53 \) nm for the 1/1 approximant. However, analysis of the bulk model structure of the 1/1 approximant [10] rules out the possibility that the observed step-terrace structure is related to bulk terminations of the 1/1 approximant structure along the high symmetry directions. The bulk truncations at high density planes of the 1/1 approximant along the [110] direction would yield a step-height distribution different to that observed. Our recent STM results on the 1/1 approximant surface perpendicular to the [001] axis [11], which is expected to be the most stable surface, are not also consistent with observed these STM images.

Similarly, no correlation is found between the observed periodic structures and the periodicities of bulk terminations of known phases along high symmetry directions. Therefore, we speculate that the observed structures may correspond to the surface projection of the known phases along non-high symmetry directions or to the unknown phases of Ag-In-Yb. However, we cannot rule out the possibility of surface reconstruction. With the available STM images and the lack of diffraction patterns, it was not possible to confirm this point.

In contrast to Sample 1, Sample 2 is found to be structurally perfect. No domain boundaries were observed in the sample of about 1 cm\(^2\) area even after annealing at 440 °C for several hours. STM images and quasicrystalline LEED patterns could be obtained from all areas of the sample. STM images and LEED patterns were similar to those observed from the primary quasicrystalline domain on Sample 1. We studied the twofold and threefold surfaces of the same system cut from
the same ingot and found no multi domains after annealing at the same temperature. The size of the twofold and threefold samples was similar to that of the fivefold sample. We also note that samples cut from different parts across the same ingot were investigated in different laboratories. All samples were found to have the same structural quality.

4. Summary
We have used scanning tunnelling microscopy to investigate the surfaces of $i$-Ag-In-Yb quasicrystals synthesized under different conditions. The sample grown at a slower rate yielded various differing structural phases on the surface. The surface of the sample grown at a faster rate is found to be structurally perfect. A systematic study should be performed to establish the possible relationship that exists between the growth conditions and the terminating surface layers. With high quality samples nowadays available, it has been possible to prepare state-of-the art surfaces. These latter are being currently analysed using various surface science techniques including ultraviolet photoemission spectroscopy and medium energy ion scattering. The progress will be reported elsewhere.

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