Bias-voltage dependent STM images from the 2–fold surface of the icosahedral Ag-In-Yb quasicrystal

Dominic Burnie¹, Sam Coates¹,², Ronan McGrath¹, and Hem Raj Sharma¹

¹Surface Science Research Centre, Department of Physics, University of Liverpool, Liverpool, L69 3BX, UK
²Department of Materials Science and Technology, Tokyo University of Science, 6 Chome–3–1 Niijuku, Katsushika City, Tokyo 125-8585

Abstract. The 2–fold surface of the icosahedral (i-)Ag–In–Yb quasicrystal has been investigated using scanning tunnelling microscopy (STM). STM data reveals a bias-voltage dependency. At high positive bias, bright protrusions are observed. At negative bias, new protrusions appear while the size of the original protrusions decreases. The STM features at both positive and negative bias polarities can be related to atomic planes intersecting the centre of Tsai-type clusters (the building blocks of the bulk structure). The bias-dependency can be explained by a change in contribution in tunnelling current from Yb and Ag/In, as expected from density of states calculations.

1. Introduction
The atomic structure of the high-symmetry (2–, 3–, and 5–fold) surfaces of the i–Ag–In–Yb system has been well-studied. The surfaces are found to be terminated at bulk planes intersecting the centre of the Tsai-type clusters, the building block of the system [1, 2, 3, 4, 5]. In the 3–fold and 5–fold cases, atomic resolution has been achieved in STM, so that specific motifs in the model can be matched to those observed by STM. Morphological dependence on bias voltage was observed on the 5–fold surface. In STM, positive sample bias probes unoccupied states and negative bias probes occupied states. Yb sites were preferentially observed on the 5–fold surface with positive bias [2], a phenomena expected due to the domination of the Yb 4d level in the unoccupied density of states [6, 7]. Likewise, achieving atomic resolution on the 3–fold surface was observed to be sensitive towards tip bias [3].

The 2–fold surface exhibits the highest atomic density of all three high-symmetry surface planes. It contains all three high-symmetry directions of the bulk vectors (i.e. 2–fold, 3–fold, 5–fold). In the previous report on 2–fold Ag–In–Yb, enhanced resolution by STM was obtained at positive bias, but no clear bias-dependency was observed [4]. In this report we show higher resolution images, where bias-dependency is clearly observed. Features seen at both positive and negative bias are linked to Ag/In–Yb model planes truncated at cluster centres.

2. Methods
The i–Ag–In–Yb quasicrystal was grown using the Bridgman method and cut perpendicular to its 2–fold rotational axis [8]. It was then polished with diamond paste (6–0.25 μm) before
washing with methanol in an ultrasonic bath. Upon insertion into an ultra–high vacuum (UHV) chamber, the surface was further cleaned with cycles of sputter–annealing. Each sputter used Ar\(^+\) for 30 minutes, before annealing at 425\(^\circ\)C for 2 hours. STM was used to probe the surface morphology. The bias voltage polarity stated in this report is with respect to the sample.

3. Results
We measured STM from the clean 2–fold Ag–In–Yb surface at various bias voltages (from +2.5 V to -2.5 V). Data was taken from the same area on the surface with the same tip condition. As such, direct comparison between each data set was possible. Here, we will discuss representative images of each bias polarity (+2.5 V and -0.8 V). These are shown in Figure 1.

At +2.5 V, a range of large protrusions displaying alignment along the 2–fold and 5–fold
Figure 2. (a) A model atomic plane intersecting the cluster centres (20 nm × 20 nm, light green: third shell Yb, dark green: glue Yb, purple: second shell Ag/In, light pink: fourth shell Ag/In and dark pink: fifth shell Ag/In). (b) Diamond motifs from the model atomic plane. (c) and (d) The corresponding diamond features in the STM images at positive and negative bias respectively.

axes are visible. This often results in the formation of diamond features with a protrusion at each vertex (highlighted in Figure 1(a) and (c)). The average small and large diagonal of the diamonds are 2.57±0.08 nm and 4.19±0.02 nm respectively. The ratio of these two values is ≈ τ (= 1.618...), the golden ratio).

At -0.8 V, the diamond features are still visible (highlighted in Figure 1(b) and (d)). Their dimensions match those at +2.5 V. Protrusions again reside at the vertices. However, their size decreases. New protrusions of comparable size and contrast appear along the diamond edges. This results in a more pronounced alignment of protrusions along the 5-fold direction.

The fast Fourier transforms (FFT) of the STM images at positive and negative bias are shown in Figure 1(e) and (f) respectively. Different coloured circles highlight spots along the three high-symmetry directions. A set of τ-scaled concentric rectangles with aspect ratio also equal to τ have been overlaid on each figure. Their scale is the same in both images. The majority of diffraction maxima are located at the vertices and edges of each rectangle, confirming the quasicrystalline 2-fold symmetry of the surface. All maxima may be indexed using the four basis vectors marked in blue in Figure 1(e) and (f). Maxima arranged along the 5-fold axes appear to have increased intensity at negative bias. This is consistent with the enhancement of protrusions along this direction by STM.

Fourier transform pass filtering the positive and negative bias STM images results in the enhancement of diamond features (Figure 1(g) and (h)). A range of diamond tiles (coloured solid black) with vertices located at the centre of protrusions have been overlaid on the +2.5 V image. The same tiles have been superimposed on the -0.8 V image. Vertices again lie at the centre of protrusions. At -0.8 V, extra diamond features are visible. Some of these are highlighted by dashed black tiles in Figure 1(h). The dashed tiles have the same size as the solid black tiles, but are shifted along the 5-fold axes such that their vertices reside along the edges of the black tiles.

We now discuss a possible explanation for the features observed by STM. This involves comparison with the model bulk structure. Figure 2(a) shows a model 2-fold Ag/In–Yb plane, formed via a bulk truncation through i–Ag/In–Yb cluster centres. Different colours correspond
to atoms belonging to different shells of the Tsai-type cluster (light green: third shell Yb, dark green: glue Yb, purple: second shell Ag/In, light pink: fourth shell Ag/In and dark pink: fifth shell Ag/In.) First shell Ag/In atomic positions have been omitted.

A set of diamond tiles displaying the same dimensions and geometry as the tiles in Figure 1(g) and (h) have been superimposed on the model plane. The vertices of the solid black tiles reside at two distinct sites: a triangle of three Yb atoms surrounding one fourth shell Ag/In atomic position and a square of four Yb atoms surrounding a fourth shell dimer. The vertices of the dashed tiles lie at sites dominated by second and fourth shell Ag/In atoms.

These observations can be explained in terms of partial density of states calculations [6, 7]. It is expected that tunnelling current contribution from Yb outweighs that for Ag/In at higher positive bias. At negative bias, the contribution from each becomes comparable [6]. This supports the suggestion that the vertices of the solid black tiles are located at Yb rich sites, resulting in the large bright protrusions observed at positive bias. At negative bias, contribution from Ag/In sites is enhanced while contribution from Yb sites is suppressed. This results in smaller protrusions at the vertices of the solid black tiles as well as additional protrusions along the diamond edges (i.e. at the vertices of the dashed tiles).

It is suggested that the bias-dependency observed here is a result of STM tip condition. Data taken using the same tunnelling conditions reported previously results in similar resolution. However, exploring a larger range of bias voltages with the bias-dependency has allowed for different features to be probed and enhanced resolution to be achieved. This has simplified the comparison with the bulk structure model.

4. Conclusions
We have shown here that STM images from the 2-fold Ag–In–Yb surface are bias voltage dependent. At higher positive bias, a range of protrusions are observed displaying alignment along the 2-fold and 5-fold axes. At negative bias, the size of the protrusions is reduced, and additional protrusions appear. The difference can be explained by enhanced contribution in tunnelling current from Yb sites over Ag/In sites at positive bias and equal contribution from both Yb and Ag/In sites at negative bias. This is expected from partial density of states calculations.

References
[1] H. R. Sharma, M. Shimoda, S. Ohhashi, and A. P. Tsai. First UHV surface studies of single-grain icosahedral Ag-In-Yb quasicrystal. 
Philosophical Magazine, 87(18-21):2989–2994, 2007.
[2] H. R. Sharma, M. Shimoda, K. Sagisaka, H. Takakura, J. A. Smerdon, P. J. Nugent, R. McGrath, D. Fujita, S. Ohhashi, and A. P. Tsai. Structure of the fivefold surface of the Ag-In-Yb icosahedral quasicrystal. Phys. Rev. B, 80(12):121401, 2009.
[3] C. Cui, P. J. Nugent, M. Shimoda, J. Ledieu, V. Fourne, A. P. Tsai, R. McGrath, and H. R. Sharma. The atomic structure of the threefold surface of the icosahedral AgInYb quasicrystal. Journal of Physics: Condensed Matter, 24(44):445011, 2012.
[4] C. Cui, P. J. Nugent, M. Shimoda, J. Ledieu, V. Fournée, A. P. Tsai, R. McGrath, and H. R. Sharma. Structure of the twofold surface of the icosahedral Ag-In-Yb quasicrystal. Journal of Physics: Condensed Matter, 26(1):015001, 2013.
[5] H. Takakura, C. P. Gómez, A. Yamamoto, M. de Boissieu, and A. P. Tsai. Atomic structure of the binary icosahedral Yb–Cd quasicrystal. Nature Materials, 6(1):58, 2007.
[6] H. R. Sharma, G. Simutis, V. R. Dhanak, P. J. Nugent, C. Cui, M. Shimoda, R. McGrath, A. P. Tsai, and Y. Ishii. Valence band structure of the icosahedral Ag-In-Yb quasicrystal. Physical Review B, 81(10):104205, 2010.
[7] Y. Ishii and T. Fujiwara. Hybridization mechanism for cohesion of Cd-based quasicrystals. Phys. Rev. Lett., 87(20):206408, 2001.
[8] C. Cui and A. P. Tsai. Growth of large single-grain quasicrystals in the Ag-In-Yb system by Bridgman method. Journal of Crystal Growth, 312(1):131–135, 2009.