Supporting Information

**Engineering Dislocation Networks for the Directed Assembly of Two-Dimensional Rotor Arrays**

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Interpretation of Scanning Tunneling Microscopy Images

A number of additional important phenomena were observed by imaging the bare Ag/Cu\{111\} system before the rotor molecules were deposited.

Figure 1. Atomically-resolved STM images of Ag on Cu\{111\} system. (A) Image of a terrace in which the position of each Ag atom in the hexagonally packed overlayer is visible. (B) Image taken at an area that was originally a Cu step edge before Ag was deposited. The left portion of the image is dominated by the upper bare Cu terrace and the right side of the image shows the Ag-covered lower terrace. Although completely covered by a continues hexagonally close packed layer of Ag atoms (as in Figure 1A), the triangles of the reconstruction in this image appear distorted due to electronic effects arising from the different packing structures of the underlying Cu. Note the larger diameter of the Ag atoms on the right side (0.28 nm) compared with the Cu atoms on the left (0.26 nm). Image Conditions: \(I = 0.55\) nA, \(V = 1\) V, \(T = 78\) K.

In Figure 1B the atoms within and surrounding the triangular domains appear distorted. Additionally, Ag atoms along the periphery of the triangle are sometimes not imaged. This is a known phenomena\(^1\,^2\) wherein the vacancies of the underlying reconstruction effect the electronic structure of overlying Ag atoms, resulting in the hcp areas imaging as depressions with seemingly ‘missing’ atoms. In the case of ‘missing’ Ag atoms the number of imaged atoms has been correlated with the size of the domain.\(^1\) Note that this phenomena does not occur under all scanning conditions and tip states, for example in Figure 1A the full Ag adlayer is observed atomically and it is obvious that the Ag monolayer is hexagonally packed and covers all areas of the reconstruction.
Figure 2. Large-scale STM image of the 1 ML of Ag on Cu{111} surface. Image Conditions: $I = 0.7 \text{nA}, V = 0.1 \text{V}, T = 78 \text{K}$.

The STM image in Figure 2 reveals that when 1 ML of Ag is deposited on Cu{111} at 300 K very large domains of the reconstruction are present on the wide Cu{111} terraces. These regions extend over very large areas; typical terraces contain ~10,000 nm$^2$ areas of the ordered structure, making this surface reconstruction an ideal template for molecular adsorption.
Figure 3. (A) Schematic showing time-averaged top view of the rotating dibutyl sulfide molecule on a Au{111} surface. (B) Rotating dibutyl sulfide molecule imaged by STM at 78 K appears as a six-lobed protrusion. (C) Different tunneling conditions reveal the surface Au atoms around the molecule. Image Conditions: (B) $V = -0.3$ V, $I = 10$ pA, (C) $V = -0.2$ V, $I = 500$ pA, Temperature = 78 K.

Thioether molecular rotors bind to the Au{111} surface through a central S atom (the axle) and the alkyl tail (rotor) interacts weakly with the surface as shown schematically in Figure 3. Both the rotor molecule and the Au surface can be imaged with atomic-scale detail. Figure 3 also shows high-resolution images of both a dibutyl sulfide molecule and the Au{111} surface below it. At 78 K the individual molecules appear as six-lobed shapes due to the time-averaging of their three equivalent orientations in the relatively slow STM scan. Imaging the system under different tunneling conditions reveals atomic resolution of the surface below the molecule, while the molecule itself appears as a depression.
Counting Statistics and Methodology

Analysis of the STM images revealed that the population of dibutyl sulfide molecules adsorbed in the hcp-overlaying Ag domains was 6.92±0.03-fold greater than the population of molecules adsorbed in the fcc-overlaying Ag region. This value was drawn from a comparison of the relative percentages of hcp-overlaid and fcc-overlaid Ag sites, shown in Table 1.

| Table 1: Relative Percentages of hcp- and fcc-Sites Occupied by Dibutyl Sulfide |
|-------------------------------|-------------------|
| hcp                          | fcc               |
| 87±3%                        | 13±1%             |

It should be noted that the relative number of available hcp and fcc sites were taken as 4:1 fcc:hcp based on the findings of Umezawa et al.,\(^4\) which is in good agreement with domain area measurements based on topographical height in STM images.

The determination of the number of dibutyl sulfide molecules adsorbed on the surface in different regions was obtained using the following methodology: A series of 30 images containing over 1,000 dibutyl sulfide molecules were analyzed. Each dibutyl sulfide molecule was assigned to either an hcp or fcc region. Molecules were considered to be bound in the fcc domain when they were imaged either as discrete units within the interstitial domain or as delocalized ‘streaks’ surrounding the hcp triangles. Molecules bound in the hcp domains were generally easy to identify by the distinctive six lobes at the center of the hcp region. Error bars were evaluated based on Poisson counting statistics.
References