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Extraordinary Atomic Mobility of Au{111} at 80 Kelvin: Effect of Styrene Adsorption

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The use of well-defined Au surfaces is ubiquitous in the fields of molecular self-assembly, molecular electronics, sensing, and catalysis studies.[1−3] Au{111} surfaces are the most commonly used in these studies because of their commercial availability, ease of preparation, and resilience to contamination. This paper describes how the presence of styrene, a weakly adsorbed molecule, dramatically restructures the Au{111} surface by binding to specific sites and lowering energetic barriers for atomic motion. The present work has important consequences for the aforementioned studies in which Au is used as a support for, or as an electrical contact to molecules. Our results indicate that one cannot assume that the atomic structure of the surface is static in the presence of weakly adsorbed molecules, even at temperatures as low as 80 K.

Au{111} has a unique structure, most commonly referred to as the *herringbone*, or more technically, the $23 \times \sqrt{3}$ reconstruction.[4,5] The lower coordination of the surface atoms in Au{111} as compared to the bulk leads to a 4.4% contraction of the top layer with 23 gold atoms stacking along the $[1\,\bar{1}\,0]$ direction that would normally contain 22 atoms in the bulk. The subsequent mismatch between the top and second layer causes domain (soliton) walls to form, which divide areas of fcc and hcp packing. The atoms contained on the soliton walls reside on bridge sites, as opposed to the other surface atoms that occupy 3-fold hollow sites. Pairs of soliton walls form a unique herringbone pattern (as seen in Figure 1) because bridge site atoms are 0.2 Å higher than the hollow site surface atoms.[4,5] The threefold symmetry of the Au{111} surface allows the pairs of soliton walls to run in three equivalent directions linked by elbows at every 120° turn. This threefold symmetry relieves stress over the whole surface, not just the direction perpendicular to the soliton wall.[6]

Because of gold's intrinsic inertness, most molecules adsorb weakly on Au and do not restructure the surface. The exception to this rule lies in molecular overlayers that form strong bonds to Au, such as thiol self-assembled monolayers, which upon adsorption convert the $23 \times \sqrt{3}$ reconstruction back to the 1×1 pattern.[7] In most experiments where Au is used to study molecules it is in either its $23 \times \sqrt{3}$ or 1×1 form, and the surface is considered to be a static lattice of atomic sites.

Previous scanning tunneling microscopy (STM) work has demonstrated that the Au{111} surface can restructure at room temperature, but only under perturbative scanning conditions.[8,9] Palmer and co-workers used STM to study bare Au{111} under "high-field" conditions ($I = 30$ nA, $V_{tip} = 1.5$ V) and observed the restructuring of herringbones, as well as the growth of thin monolayer high gold islands (so-called "fingers") from step edges at room temperature.[8,9] The authors explained that this atomic motion originated from electric-field-induced atom detachment from step edges. The authors also noted that under "low-field" conditions (<0.1 nA, <1.0 V), the surface showed no restructuring after prolonged periods of scanning. Movement of the herringbone reconstruction on bare Au{111} was also reported by Avouris and co-workers, but only after they removed surface atoms with the STM tip.[10] The effect was explained in terms of motion of surface atoms in order to minimize stress around the defect created by the tip.[10]

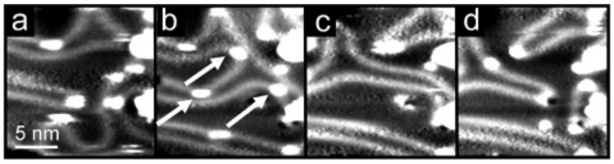

Figure 1. Time-lapse STM imaging of 0.03 ML styrene on Au{111} at 80 K. Soliton walls appear as raised lines and their positions change over time. Image conditions: $-0.6\ V_{tip}$, $I = 2$ pA. The time between each image is approximately 4 min.

In this paper we present STM results that demonstrate that the presence of styrene, a weakly adsorbed molecule (~60 kJ/mol),[11] allows dramatic restructuring of the Au{111} surface to occur at 80 K and under "ultralow-field" scanning conditions. All images tracking surface reconstruction were recorded at $I = 2$ pA and $V_{tip} = -0.6$ V to minimize any influence of the tip.

The effect of styrene adsorption on the structure of the Au{111} surface was studied by time-lapse STM imaging at 80 K. Figure 1 shows a set of four representative images, taken from a series of 152 images recorded over 2.5 h, of 0.03 monolayers (ML) of styrene adsorbed on Au{111}. The pairs of raised lines are the soliton walls of the herringbone reconstruction of Au{111}, and the raised circles (three of which are highlighted by white arrows in Figure 1b) are individual styrene molecules adsorbed at the elbows of the herringbone reconstruction. Two protrusions, each consisting of a clump of several styrene molecules, on the right-hand side of the four images serve as "landmarks" that demonstrate that the images are of the same area of the surface. These images demonstrate that at temperatures as low as 80 K, and while scanning under ultralow-field conditions ($-0.6\ V_{tip}$, 2 pA), the presence of styrene causes motion of the soliton walls to occur. Our control experiments show this same restructuring was not observed at 80 K in the absence of styrene under the same gap conditions (see Supporting Information).

In addition to motion of the herringbones we also observed that the presence of styrene dramatically alters the shape of Au terraces and islands. Figure 2 shows two STM images of 0.03 ML of styrene on Au{111} at 80 K taken from a set of 400 images. The elevated areas of both images are Au terraces, one atomic layer high. It is clear from these images that over the course of 2.7 h, the Au islands in the center of the image have reduced in size (white arrows in Figure 2a) and gold fingers (white arrows in Figure 2b) have grown out from the upper terrace. The Au fingers have a width of 5 nm and a height of 0.24 nm, corresponding to the height of a single Au atom and in exact agreement with those reported by Palmer and co-workers.[8,12] Rearrangement of the herringbone reconstruction is also observed in Figure 2. It is clear from these data that the presence of styrene lowers the energetic barriers for both atom

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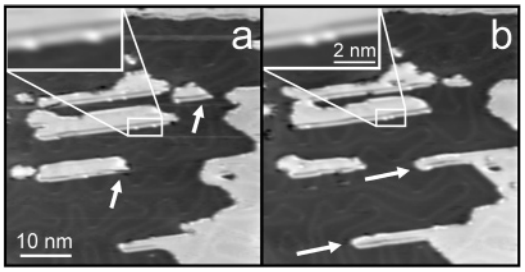

Figure 2. Two STM images taken 2.7 h apart (0.03 ML styrene on Au{111} at 80 K) showing the growth of one atomic layer high gold islands, so-called "fingers" (white arrows in Figure 2b). Depletion of atoms from the highlighted Au islands is shown by the white arrows in Figure 2a. Inset shows the motion of styrene molecules adsorbed at the top of step edges. Image conditions: $V_{\text{tip}} = -0.6$ V, $I = 2$ pA.

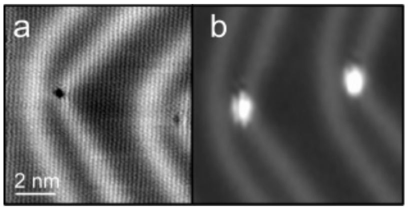

Figure 3. (a) STM image of atomic resolution of bare Au{111} before styrene is deposited. Edge dislocations (depressions) are present at the elbows of the herringbone reconstruction. Figure 3b shows an equivalent area after styrene deposition in which styrene is imaged as a protrusion. Conditions: (a) $V_{\text{tip}} = -0.5$ V, $I = 100$ pA; (b) $V_{\text{tip}} = -0.6$ V, $I = 80$ pA.

detachment from step edges and for movement of the herringbone reconstruction.

To investigate the mechanism by which styrene promotes surface restructuring, we studied the adsorption site of styrene. Our data show that styrene preferentially adsorbs at sites above step edges and also at the elbows of the herringbone reconstruction. The insets of Figure 2 parts a and b show that styrene molecules adsorb above the step edge and that they are mobile. Atom detachment from step edges is the rate-limiting step for the motion of step edges and for island rearrangement.[13] Therefore, we postulate that the presence of styrene molecules above the step edges lowers the energetic barrier for Au atom detachment from the step edges by stabilizing the transition state that involves a Au atom in a low-coordination state.[14,15] Due to the Smoluchowski effect, step edges have electron depleted areas above them and electron rich areas below.[16] The fact that styrene adsorbs preferentially above the step edges means that styrene, like benzene, acts like a nucleophile and therefore can donate charge to Au atoms and stabilize them as they detach from step edges.[17]

Figure 3 illustrates how styrene also preferentially adsorbs at the elbows of the herringbone reconstruction where edge dislocations are present. Figure 3a shows an STM image of two atomically resolved edge dislocations on a bare Au surface. Edge dislocations are areas of a surface where an atomic row is missing and locally two atomic rows must meet up with three rows, leaving coordinatively unsaturated atoms. Our data show that edge dislocations are present on one of the soliton walls at every elbow of the herringbone reconstruction. Figure 3b shows an area equivalent to that in 3a after deposition of 0.03 ML of styrene. It is clear that the edge dislocations serve as nucleation centers for adsorption of styrene.[18]

For an explanation of how the herringbone reconstruction moves we turn to a similar system consisting of 2 ML of Cu on Ru{0001}.[19,20] Extensive simulations and experiments have been performed and show that this system also has a mismatch between the top and second atomic layers resulting in the formation of pairs of soliton walls.[19,20] Data from these studies reveal that the greatest energetic barrier to motion of a soliton wall is not the movement of the straight part of the soliton wall, but the propagation of the edge dislocation present at the elbow across the surface, and that this barrier is of the order 1 eV.[19] This is why, even at room temperature, motion of the herringbone reconstruction is not observed, except under perturbative scanning conditions.[8,9] As we only observe the motion of the herringbones when styrene is present, we postulate that the presence of a styrene molecule adsorbed above the edge dislocation allows the position of the edge dislocation to move across the surface by interacting favorably with the coordinatively unsaturated atoms there.

To summarize, our findings point toward the fact that the Au{111} $23 \times \sqrt{3}$ surface is constantly restructuring in the presence of styrene, even at 80 K. Styrene preferentially adsorbs at specific locations on the surface and assists in atom extraction from step edges, as well as lowering the energetic barrier for movement of the herringbone reconstruction. These results have important implications for work in which the Au{111} surface is used as a support for or contact to molecules. Work is currently underway to investigate the effect of both temperature and molecules with different chemistries on these phenomena.

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Supporting Information Available: STM movies showing the mobility of atomic steps and herringbones in the presence of styrene, control movies of bare Au{111} taken at 80 K (mpg and jpg), a high-resolution image of styrene adsorbed at the top of atomic step edges, and sample preparation methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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