Molecular Adsorption Behavior on an Au(111) Surface(STM-other surfaces)

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Molecular Adsorption Behavior on an Au(111) Surface

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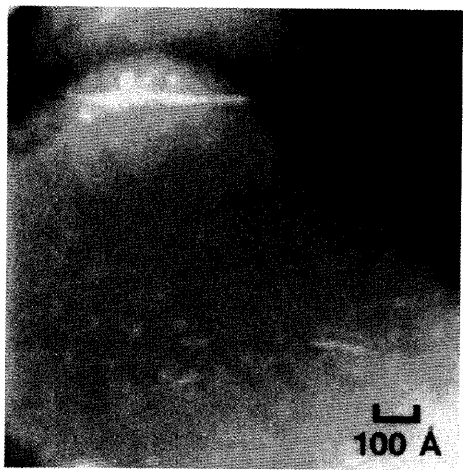
Scanning tunneling microscopy (STM) was used to study molecular adsorption behavior on reconstructed Au(111) surface. The STM images of ethyl 4-[2-(2-pyrazyl)ethenyl]cinnamate (E25PC) molecules adsorbed on Au(111) revealed ordered nucleation of molecular islands at the initial growth stage. The islands grew with spacing 38 Å in rows 77 Å apart. The periodicity of 38 Å × 77 Å corresponds to that of STM images of bare Au(111) reconstructed surface in air. The behavior of molecules adsorbed on Au(111) is discussed from a view point of Au(111) herringbone reconstruction.

KEYWORDS: Au(111), molecular adsorption, ordered nucleation, herringbone structure, scanning tunneling microscopy

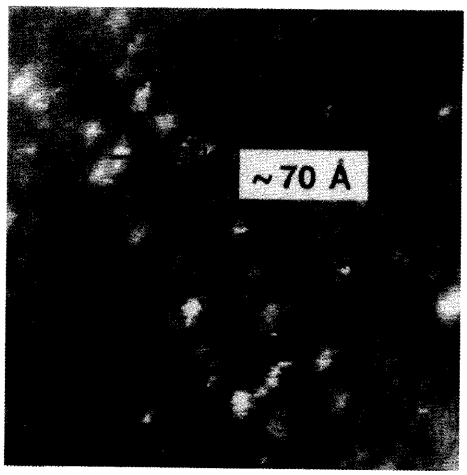
1. Introduction

In the molecular adsorption mechanism, the reconstruction of the surface on which molecules are adsorbed plays an important role. It is important to investigate the reconstructed structure and its influence on molecular adsorption. Gold is the only fcc metal whose surface exhibits closed-packed (111) reconstructed structure. The reconstruction of Au(111) has been widely studied by LEED [1], RHEED [2], TEM [3, 4] and STM [5, 6]. Recently, detailed structures of the Au(111) reconstructed surface were studied by using STM with atomic resolution [6], and it was confirmed that the Au(111) surface exhibits the long-range $22 \times \sqrt{3}$ reconstructed structure, usually referred to as a "herringbone" structure. In the $22 \times \sqrt{3}$ reconstructed surface, the outermost atomic layer is contracted laterally along one of the three (1-1 0) direction, in order to relieve the anisotropic stress that would be present on the unreconstructed surface. The misfit between the outermost layer and the bulk leads to periodic pairwise-arranged partial dislocations, which separate alternating regions with fcc-type stacking and hcp-type stacking. The dislocation lines appear as higher ridges in the STM images. In a recent UHV-STM study of the Au(111) reconstructed structure by Hasegawa *et al* [7, 8], pairs of partial dislocation lines separated by 44 Å with a periodicity of 63 Å and a height of 0.1 to 0.2 Å was observed. The $22 \times \sqrt{3}$ unit cell of herringbone structure contains 23 surface atoms, allowing a 4.4 % contraction along the (1-1 0) direction in the topmost layer. The width of the fcc region is wider than that of the hcp region, because the fcc structure is enegitically more favored. Although the $22 \times \sqrt{3}$ reconstruction relieves the surface stress along the (1-1 0) direction, it still remains in other directions. To relieve the residual stress, surface superstructure is occationally formed consisting of a regular alternation of uniaxial domains arranged in a zigzag pattern [7, 8].

It is notable that the $22 \times \sqrt{3}$ reconstructed structure also exists in air. Mizutani *et al.* observed the reconstructed Au(111) surfaces in air and reported the widen-



(a)



(b)

Figure 1. STM images of Au(111) thin film deposited on a mica substrate obtained at 0.8 V, 0.20 nA. (a) The characteristic herringbone dislocation lines are observed. (b) Another superstructure perpendicular to the herringbone line can be seen.

ing of the spacing of the dislocation lines and disappearance of the reconstruction [9]. They suggested that according to the adsorbates such as water and contaminants, the surface atoms will recover the deficiency of the coordination number and the contractive stress in the surface layer is relieved, resulting in the widening of the spacing.

However, in our previous work, we proposed the existence of the another reconstructed superstructure perpendicular to the herringbone structure in air [10]. Figure 1 shows STM images of an Au(111) thin film deposited on a mica substrate. Figure 1(a) is a large-size STM image (1000 Å × 1000 Å) showing the Au(111) herringbone dislocation lines separated by 70 Å. Figure 1(b) is a magnified image of Fig. 1(a) showing the detailed herringbone structure. The herringbone line is composed of brighter spots arranged at almost regular intervals, 35 Å. This indicates that the Au(111) surface exhibits the reconstructed structure in air with a periodicity of 70 Å × 35 Å.

On the other hand, the arrangement of the molecules adsorbed on Au(111) is strongly affected by the reconstructed structure of Au(111). In our previous paper [11], we reported that the STM images of 1,4-bis [β-pyridyl-(2)-vinyl]benzene (P2VB) molecules adsorbed on an Au(111) surface showed well-ordered molecular monolayer with a periodicity of 6.8 Å × 35 Å. It was observed that the periodicity along a axis (35 Å) was much larger than that obtained by the X-ray diffraction data for its bulk structure. The widening of the periodicity indicates the molecular rearrangement of P2VB strongly influenced by the reconstruction of Au(111).

In this work, in order to clarify the reconstruction of Au(111) and its relation to the molecular adsorption process on it, we investigate the molecular adsorption behavior of ethyl 4-[2-(2-pyrazyl)-ethenyl]cinnamate (E25PC) on an Au(111) surface. The STM images reveal the ordered molecular nucleation on an Au(111) surface, which was not observed in the case of P2VB adsorption.

2. Experimental

A mica substrate cleaved in pure water was heated to 420°C and annealed for 2 h in order to remove residual contaminants, after it was introduced to high-vacuum chamber. Gold was evaporated onto the mica substrate from a resistively heated tungsten-boat. During Au deposition, the pressure was less than 5×10^{-6} Torr. After the deposition, the sample was gradually cooled to room temperature and exposed to air. X-ray diffraction studies have shown that Au thin films prepared under these conditions form (111) crystallites [12].

E25PC molecules were evaporated from an Al_2O_3 crucible onto an Au thin film maintained at 20°C. During deposition, the pressure was less than 2×10^{-6} Torr.

The STM used was a Nanoscope II (Digital Instruments, Inc.). Images were acquired in air at room temperature using PtIr tip. The typical tunneling current and sample bias voltage were 0.2–0.5 nA and 0.8 V. The images were not sensitive to the sample bias voltage.

3. Results and Discussion

Figures 2 are STM images of E25PC molecules adsorbed on Au(111) at room temperature, revealing the ordered nucleation of molecular islands at the initial growth stage. Ordered rows of islands with nearly uniform spacing are observed on every wide terrace. The rows are separated by 77 Å and the spacing within a row is 38 Å on average. The arrays of nuclei are aligned in three equivalent orientations related by 120° rotaions. It is also observed that there are differently oriented domains on the same terrace as shown in Fig. 2(b).

(a)

(b)

Figure 2. STM images of E25PC island arrays on Au(111) obatained at (a) 0.8 V, 0.20 nA and (b) 0.8 V, 0.30 nA. (a) The scan size is 1350 Å × 1350Å. (b) The scan size is 1580 Å × 1580Å

Table 1
The periodicity of reconstructed structures.

reconstruction	periodicity
Au(111) reconstruction in air [10]	70 Å × 35 Å
E25PC on Au(111)	77 Å × 38 Å
SAM on Au(111)	73 Å × 140 Å
Ni on Au(111)	73 Å × 140 Å

It should be noted that the periodicity of E25PC nuclei adsorbed on Au(111) nearly coincides with that of the bare Au(111) reconstructed structure in air (Table I) [10], indicating that the Au(111) surface surely exhibits the new reconstructed structure. Our experimental results are qualitatively explained as follows. In an unreconstructed Au(111) surface, the surface layer tends to contract in order to compensate for its reduced coordination. The adsorbed molecules are inclined to compensate for deficiency of the coordination number of the surface atoms. In this way, molecular adsorption induces the reduction of the surface stress which stabilizes the reconstructed structure.

This type of ordered nucleation has already been confirmed in the case of metal (Ni) [13–15] or self-assembled monolayer (SAM) molecules [16] deposited on Au(111). It was suggested that the nucleation sites of metal or SAM are located at the bending points of the herringbone zigzag pattern on Au(111). It is impossible at this stage to decide whether the E25PC nuclei are located on such sites in the same way, because our STM images cannot resolve both the reconstruction pattern and the molecular adsorption sites with atomic resolution, and because the periodicity of E25PC nuleation is much shorter compared with that of metal or SAM nucleation on Au(111) (Table I).

The reconstruction of the Au(111) surface is formed by the reduction of the surface stress. Therefore, the reconstructed structure is strongly affected by the factors that modify the distribution of the surface stress, such as molecular adsorption process. The variety of the periodicity in Tabal I is caused by the difference in the surface stress distribution modified by adsorption process. We suggest here that molecular adsorption process induces the reduction of the surface stress and the reconstruction of the Au(111) surface.

4. Conclusion

The STM images of E25PC molecules adsorbed on an Au(111) surface reveal the well-ordered nucleation arrays with a periodicity of 77 Å × 38 Å. The adsorption process is considered to induce the long-range reconstruction of the Au(111) surface. A clear understanding of molecular adsorption behavior will be obtained through the STM observations under various deposition conditions such as deposited species, substrate temperatures, deposition rates and coverages.

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