

Scanning Tunneling Microscopy Observations of Sulfur Adsorbates on Pd (111) Surface

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Abstract—The adsorption behaviors of sulfur atoms on Pd (111) surface have been investigated by Scanning Tunneling Microscopy (STM). After the clean Pd (111) surface is exposed to different doses of H₂S at room temperature. The direct STM results of one monolayer adsorption show the terraces of Pd surface are dominated by $\sqrt{3} \times \sqrt{3}R30^\circ$ Pd (111)-S while a mixture of small area of $\sqrt{7} \times \sqrt{7}R19^\circ$, disordered S and $5\sqrt{3} \times 2$ stripes distributes along the step edges. Excess one monolayer adsorption results in minor change for the proportion of different structures. The evolution of S induced reconstruction with the annealing temperature are also investigated by STM. After annealing to 370K, most of $\sqrt{3} \times \sqrt{3}R30^\circ$ reconstruction on the terrace are converted into $\sqrt{7} \times \sqrt{7}R19^\circ$. Heating to 420K and 470K favors the missing of more and more sulfur atoms at the area of $\sqrt{3} \times \sqrt{3}R30^\circ$ while no obvious change occurs in the $\sqrt{7} \times \sqrt{7}R19^\circ$ area. The corresponding models are given for three observed ordered reconstruction structures.

Index Terms—scanning tunneling microscopy, sulfur, palladium, heating, reconstruction

I. INTRODUCTION

The catalytic activities of various metal surfaces have been the subject of numerous investigations. Of particular interest is Pd for its utility in catalysts for various reactions [1]-[6]. Sulfur is a well known poison to Pd catalysts [7]-[12]. It is reported that even the presence of a small amount of sulfur compounds can lead to deactivation of Pd [13], [14]. To obtain the insight into the underlying mechanism, S adsorption on well-defined, low-index Pd surfaces, especially on a Pd (111) surface, has been investigated by various surface science techniques [15]-[18]. Although several coexisting ordered phases have been found in the Pd (111)-S system at room temperature [19], the direct observation of the proportion of these phases on Pd surface as a function of temperature is still lack.

In this paper, we report a Scanning Tunneling Microscopy (STM) study on an S-adsorbed Pd (111) surface prepared by exposing to H₂S at room temperature. The exposure of the clean Pd (111) surface to 1.0 L and 3.0L of H₂S causes one mono-layer and excess one

mono-layer of sulfur atoms on the surface. The high resolution STM images clearly show that the terraces of the Pd surface are dominated by $\sqrt{3} \times \sqrt{3}R30^\circ$ Pd (111)-S while a mixture of $\sqrt{7} \times \sqrt{7}R19^\circ$, disordered S and $5\sqrt{3} \times 2$ stripes distributes along the step edges. The evolution of S induced reconstruction with the annealing temperature is also investigated by STM.

II. EXPERIMENT

The experiments were carried out in a multi-chamber Ultrahigh Vacuum (UHV) system housing a SPECS variable temperature STM with base pressure of less than 2×10^{-10} mbar.

The Pd (111) surface was cleaned by several Ar+ sputter (1.5keV, 4.8-5.0 μ A, 45 min) and anneal (900K, 10 min) cycles. The adsorption of sulfur onto the surface was performed by exposing the clean Pd (111) surface to H₂S (purity 99.999%) in the STM chamber at room temperature. It is well established that H₂S molecules dissociate on a Pd (111) surface at room temperature and left the sulfur atoms on the surface.

STM images were acquired at room temperature with a chemically etched W tip. Positive voltage indicates that the samples were biased positively with respect to the tip.

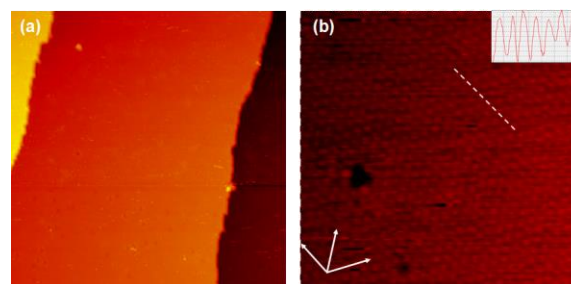


Figure 1. STM images of a clean Pd (111) surface. (a) A large area image, 600 Å × 600 Å, $V_t = -2433.4$ mV, $I_t = -0.03$ nA. (b) A atomic resolution image, 70 Å × 70 Å, $V_t = -540.8$ mV, $I_t = -0.04$ nA. Inset: the profile measurement along the white dot line. V

III. RESULTS AND DISCUSSION

A. Clean Pd (111) Surface

Fig. 1(a) shows a typical STM image for a Pd (111) surface. The quality of Pd (111) surface can be further checked from the high resolution image in Fig. 1(b). Pd

atoms are ordered along $[\bar{1}10]$ directions, i.e., three equivalent, close-packed directions (see white arrows). The distance between two neighbored Pd atoms along the white dot line is measured as 2.75Å, while the corrugation of Pd atom is about 2 pm from the inset. In addition, a few defects can be found on the surface. The black hole in Fig. 1(b) corresponds to the defect caused by missed Pd atoms.

B. One Mono-Layer S Adsorption on Pd (111) Surface

To obtain the insight into the real structure for sulfur poison mechanism the S/Pd (111) adsorption of one mono-layer is considered. After the H₂S exposure of 1 Langmuir (L) (1L = 10⁻⁶Torr s, 1Torr = 133Pa) at room temperature, the Pd (111) surface is mostly covered by sulfur atoms both on the terrace and along the edge of steps and defects.

Fig. 2 shows the STM images and corresponding models on the terrace. When inspecting the large-area image in Fig. 2(a) by eye, $\sqrt{3} \times \sqrt{3}R30^\circ$ structure has a proportion of more than 75%. Fig. 2(b) is the high-resolution image of square area in Fig. 2(a). In details, the distance of adjacent $\sqrt{3} \times \sqrt{3}R30^\circ$ S atoms is 4.78Å (the distance for two neighbored Pd atoms is 2.75Å). The angle between the lattice direction of Pd (111) and S is 30°. Both distance and angle are in satisfactory agreement with the $\sqrt{3} \times \sqrt{3}R30^\circ$ structure. Based on these values a simple model of $\sqrt{3} \times \sqrt{3}R30^\circ$ structure is given in Fig. 2(c). Gray circles represent Pd atoms, yellow circles S atoms. The white rhombus indicates the unit cell. For $\sqrt{3} \times \sqrt{3}R30^\circ$ all S atoms occupy the threefold FCC sites of Pd (111) surface.

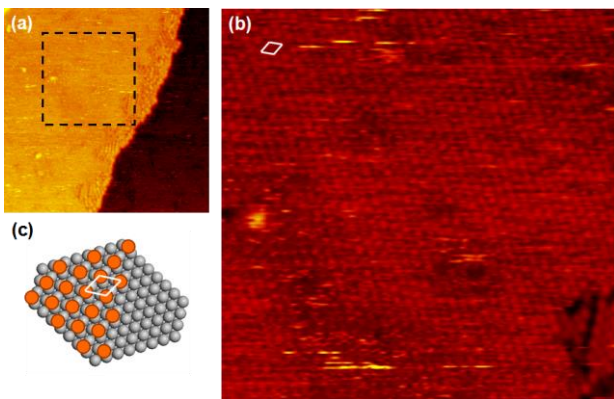


Figure 2. (a) Large-area STM image of S/Pd (111), 360Å×360Å, Vt= -2288.5mV, It= -0.03nA. (b) is the high-resolution image of square area in Fig. 2(a). 160Å×160Å, Vt= -2288.5mV, It= -0.03nA. (c) Model for the $\sqrt{3} \times \sqrt{3}R30^\circ$ structure. Gray circles represent Pd atoms, yellow circles S atoms. The white rhombus indicates the unit cell.

Fig. 3 shows the STM images and corresponding models on the step edge. Obviously the edge is decorated by coexisting $\sqrt{7} \times \sqrt{7}R19^\circ$, disordered S, stripes in Fig. 3(a). The models for these order structures are given in Fig. 3 (b)~Fig. 3(d) respectively. Gray and black circles represent Pd atoms, yellow circles S atoms. The white rhombus and green rectangle indicate the unit cell.

In the middle of Fig. 3(a), two types of $\sqrt{7} \times \sqrt{7}R19^\circ$ structures are observed. The distance is measured as 7.22Å. The rotation angle is + and -19° with respect to the Pd (111) lattice. By comparing with the previous report of $\sqrt{7} \times \sqrt{7}R19^\circ$ [19], a mixed layer model with two S atoms and three Pd atoms in the unit cell is considered in Fig. 3(b) and Fig. 3(c). Large yellow circles are S atoms on FCC sites. Small yellow circles are S atoms on HCP sites. Small black circles are Pd atoms in the mixed layer.

In the lower right corner of Fig. 3(a), there exist several parallel stripes separated by dark lines. The stripes on the S/Pd (111) surface have a width of two to four atoms. The proportion of three-atom-width stripe is more than 80%. In Fig. 3(a) the rectangle indicates the unit cell for three-atom-width stripe structure. The lattice constants are measured as 5.49Å and 23.7Å. They are 2 and $5\sqrt{3}$ multiple of lattice constants (2.75Å) of Pd (111) surface. Furthermore all stripes run along $[\bar{1}10]$ directions. The details match well with $5\sqrt{3} \times 2$ rect-S pattern in Fig. 3(d). The gray circles are Pd atoms. Every fifth row of the topmost Pd layer is missing. The yellow circles are S atoms. The translucent yellow circles are S atoms in the troughs.

However the 2×2 structure from other reports [19] has a similar stripe topography with the $5\sqrt{3} \times 2$ rect-S structure in our study. The distinction between them is the length/width ratio of the green rectangle in Fig. 4(a). For 2×2 structure the ratio is $\sqrt{3}:1$. But from Fig. 4(a) the ratio is measured as 1:1 corresponding to $5\sqrt{3} \times 2$ rect-S structure.

In the lower right corner of Fig. 3(a), no periodic structure is obvious which is named as a disordered S area.

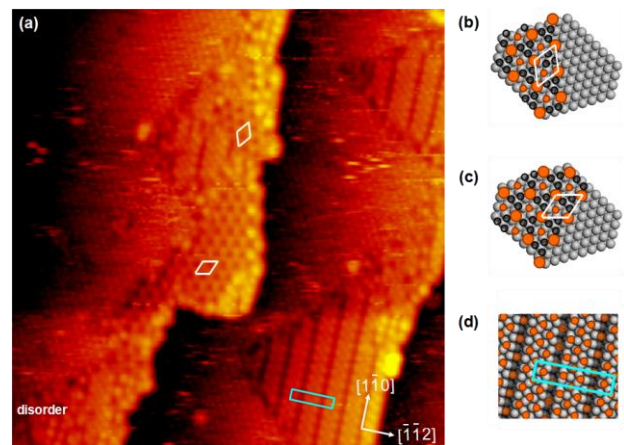


Figure 3. (a) A large-area STM image of S/Pd (111), 240Å×240Å, Vt= -1962.9mV, It= -0.04nA. (b) and (c) are models for the $\sqrt{7} \times \sqrt{7}R19^\circ$ structure. (d) is model for the $5\sqrt{3} \times 2$ structure. Gray circles represent Pd atoms, yellow circles S atoms. Black circles represent Pd atoms of mixed layer. The white rhombus and green rectangle indicate the unit cell for these structures.

After H₂S exposure of 3L on Pd (111) surface, only a few and small patches as the second layer are found

indicating that the surface becomes inert after approximately one layer of S. The four components are still observed despite the proportion of decorating species is increasing slightly.

In a word, in our research for deposition of H_2S on Pd (111) at room temperature, the terraces of Pd surface are dominated by $\sqrt{3}\times\sqrt{3}R30^\circ$ Pd (111)-S while a mixture of small area of $\sqrt{7}\times\sqrt{7}R19^\circ$, disordered S and $5\sqrt{3}\times 2$ stripes distributes along the step edges. It helps to explain that the predominant LEED pattern is $\sqrt{3}\times\sqrt{3}R30^\circ$ but not $\sqrt{7}\times\sqrt{7}R19^\circ$ [19].

C. The Structure of S/Pd (111) after Annealing

After the H_2S exposure of 3L on Pd (111) at room temperature, the sample was annealing to different temperature. After annealing to 370K, the significant changes on the structures have been found in Fig. 4. Most of the initial $\sqrt{3}\times\sqrt{3}R30^\circ$ reconstructions have been converted into $\sqrt{7}\times\sqrt{7}R19^\circ$ in Fig. 4(a) or $\sqrt{7}\times\sqrt{7}R-19^\circ$ in Fig. 4(b) although a small portion of $\sqrt{3}\times\sqrt{3}R30^\circ$ is left in the lower right corner of Fig. 4(a). It is worth noting that the steps are still decorated by disordered S structures. Therefore, the whole surface can be described as the mixture of the intact $\sqrt{7}\times\sqrt{7}R19^\circ$, the damaged $\sqrt{3}\times\sqrt{3}R30^\circ$ and the disordered area. This finding is consistence with the previous LEED observations: the predominant LEED pattern changes from $\sqrt{3}\times\sqrt{3}R30^\circ$ to $\sqrt{7}\times\sqrt{7}R19^\circ$ after heating to 370K [19].

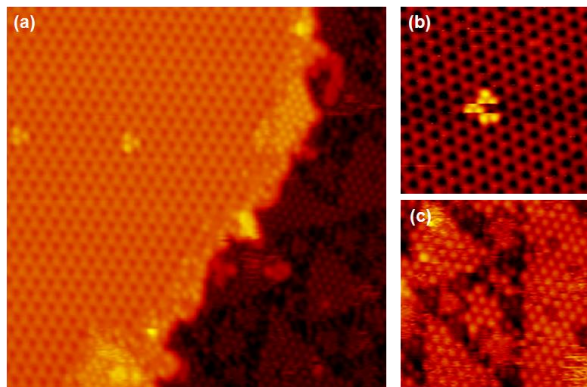


Figure 4. STM images of the S/Pd (111) surface after annealing to 370K. (a) $200\text{\AA}\times 200\text{\AA}$, $V_t = -1790.1\text{mV}$, $I_t = -0.04\text{nA}$. (b) $85\text{\AA}\times 85\text{\AA}$, $V_t = -1062.3\text{mV}$, $I_t = -0.04\text{nA}$. (c) $85\text{\AA}\times 85\text{\AA}$, $V_t = -1790.1\text{mV}$, $I_t = -0.03\text{nA}$.

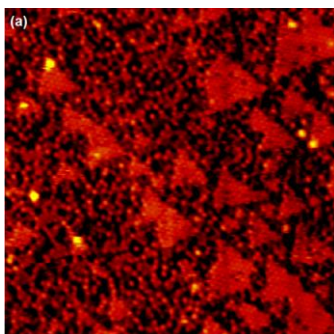


Figure 5. STM images of the S/Pd (111) surface after heating to 420K and 470K. (a) Heating to 420K, $300\text{\AA}\times 300\text{\AA}$, $V_t = -1846.0\text{mV}$, $I_t = -0.03\text{nA}$. (b) Heating to 470K, $300\text{\AA}\times 300\text{\AA}$, $V_t = -1962.9\text{mV}$, $I_t = -0.04\text{nA}$.

After the S/Pd (111) sample is annealing to 420K and 470K, the STM observations show that no obvious change occurs in the the $\sqrt{7}\times\sqrt{7}R19^\circ$ and $\sqrt{7}\times\sqrt{7}R-19^\circ$ area. However, as shown in Fig. 5, the domain size of the $\sqrt{3}\times\sqrt{3}R30^\circ$ area becomes smaller due to the missing of more sulfur atoms.

IV. SUMMARY

The Reconstruction of a Pd (111) surface exposed to H_2S at room temperature has been investigated by STM. After the adsorption of one mono-layer of sulfur on the surface, the $\sqrt{3}\times\sqrt{3}R30^\circ$ dominate mainly the terraces while the step edges are occupied by a mixture of $\sqrt{7}\times\sqrt{7}R19^\circ$, disordered S and $5\sqrt{3}\times 2$ stripes. The annealing process at 370K converts the $\sqrt{3}\times\sqrt{3}R30^\circ$ areas on the terraces into $\sqrt{7}\times\sqrt{7}R19^\circ$ and lefts small areas of the damage of $\sqrt{3}\times\sqrt{3}R30^\circ$ and disordered S.

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