

Adsorption and Wetting Structures of Kr on Pt(111) at 8 K and 45 K Studied by Scanning Tunneling Microscopy

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(Received March 8, 2001; accepted for publication March 27, 2001)

Adsorption and wetting structures of Kr on Pt(111) were studied using scanning tunneling microscopy. The characteristics were different from those of Xe/Pt(111) and Xe/Cu(111). At 8 K, Kr atoms adsorbed on terraces and preferential adsorption to step edges was not observed. Kr atoms were imaged with 0.12 nm height and 1.0 nm full width at half maximum. With the additional exposure, adsorption at step edges occurred, with a slight preference for the upper step edges. However, no evidence for the characteristic properties, such as repulsive interaction between adsorbates or modification of the electronic structures at step edges, was observed. With the rise in temperature to 45 K, Kr atoms on the terraces increased in size with hexagonal shape, and wetting of the step edges began. In the wetting process, the lower step edge was more preferential, and the wetting region on both step edges grew with a stripe shape; the edge of the wetting region was not irregular but straight and parallel to the steps. In addition, the height of the Kr images decreased and showed two different values, namely, Kr stripes grown from the lower step edges were observed to have 0.10 nm height, 0.02 nm higher than those with a height of 0.08 nm grown on terraces or at upper step edges. The obtained results indicate the existence of two different structures, which may be attributed to the two structures previously observed by the macroscopic analyses.

KEYWORDS: STM, Kr, Pt(111), adsorption, terrace, step edge, wetting

1. Introduction

Since rare gas atoms have a simple closed shell electronic structure, they have been widely used as ideal two-dimensional model systems to clarify the wetting process of solid surfaces.^{1–12} Structural aspects have been basically investigated using reciprocal space methods in the past: low-energy electron diffraction,¹ spin-polarized low-energy electron diffraction,² He diffraction,³ elastic and inelastic He-scattering and so on.⁴ However, in the wetting process, microscopic structures such as steps or defects have been considered from the beginning to play important roles. Recent scanning tunneling microscopy (STM) studies on an atomic scale revealed the existence of interesting characteristics during the initial adsorption and growth processes of the rare gases on metal surfaces.

For example, Xe atoms on Pt(111) and Cu(111) surfaces show completely different behaviors at step edges.^{5–12} Namely, Xe atoms on the Pt(111) surface are preferentially adsorbed on the upper step edges which results in the formation of one-dimensional (1D) chains of Xe atoms. These chains lead to a local repulsive interaction with subsequent Xe adatoms, and Xe atoms do not serve as nuclei for the formation of two-dimensional (2D) islands at the upper step edges. With increasing coverage, Xe islands grow from the lower step edges to the lower terraces. On the other hand, Xe atoms on the Cu(111) surface are preferentially adsorbed at the lower step edges and form 1D chains. Along the chains, the interaction between Xe atoms is repulsive. Once Xe atoms occupy the lower step edges, they modify the Ehrlich-Schwoebel barrier, resulting in wetting at the upper step edges

with attractive interaction.

Therefore, despite the stable electronic structure of the rare gas atoms, their initial adsorption characteristics on metals are complex, and their mechanism has not been clarified completely. In order to further investigate the characteristics of the rare gases on metals, we investigated the adsorption and wetting processes of Kr on the Pt(111) surface on an atomic scale using STM, and the results were compared with those obtained for the cases of Xe/Pt(111) and Xe/Cu(111).

2. Experiments

A Pt single crystal was prepared by repeated argon ion sputtering (770 K) and annealing (~ 1400 K) cycles. Carbon contamination on the surface was removed by annealing at 1100 K in an O₂ environment ($\sim 1 \times 10^{-5}$ Pa). The base pressure was 7×10^{-9} Pa. An electrochemically etched tungsten tip was used. Krypton dosing was performed using an electronically controlled pulse valve. In order to eliminate the influence of the environmental effect, the STM tip was extracted during the Kr dose. Therefore, observation of the same place was difficult, but reproducibility was confirmed by repeating the experiment. According to the results of the diffraction measurement, Kr atoms are mobile at 25 K on the Pt(111) surface and form islands,⁶ and annealing up to 50 K improves the order slightly. Therefore, in this study, Kr atoms were adsorbed at 8 K first, and change due to annealing at 45 K was observed. The sample temperature was monitored using an Au+0.07%Fe-Cr thermocouple located near the sample.

3. Results and Discussion

Figure 1 shows a series of STM images with different Kr coverages at 8 K. As evident in Fig. 1(a), Kr atoms were adsorbed on the Pt(111) terraces, and they were imaged with 0.12 nm height and 1.0 nm full width at half maximum (Fig.

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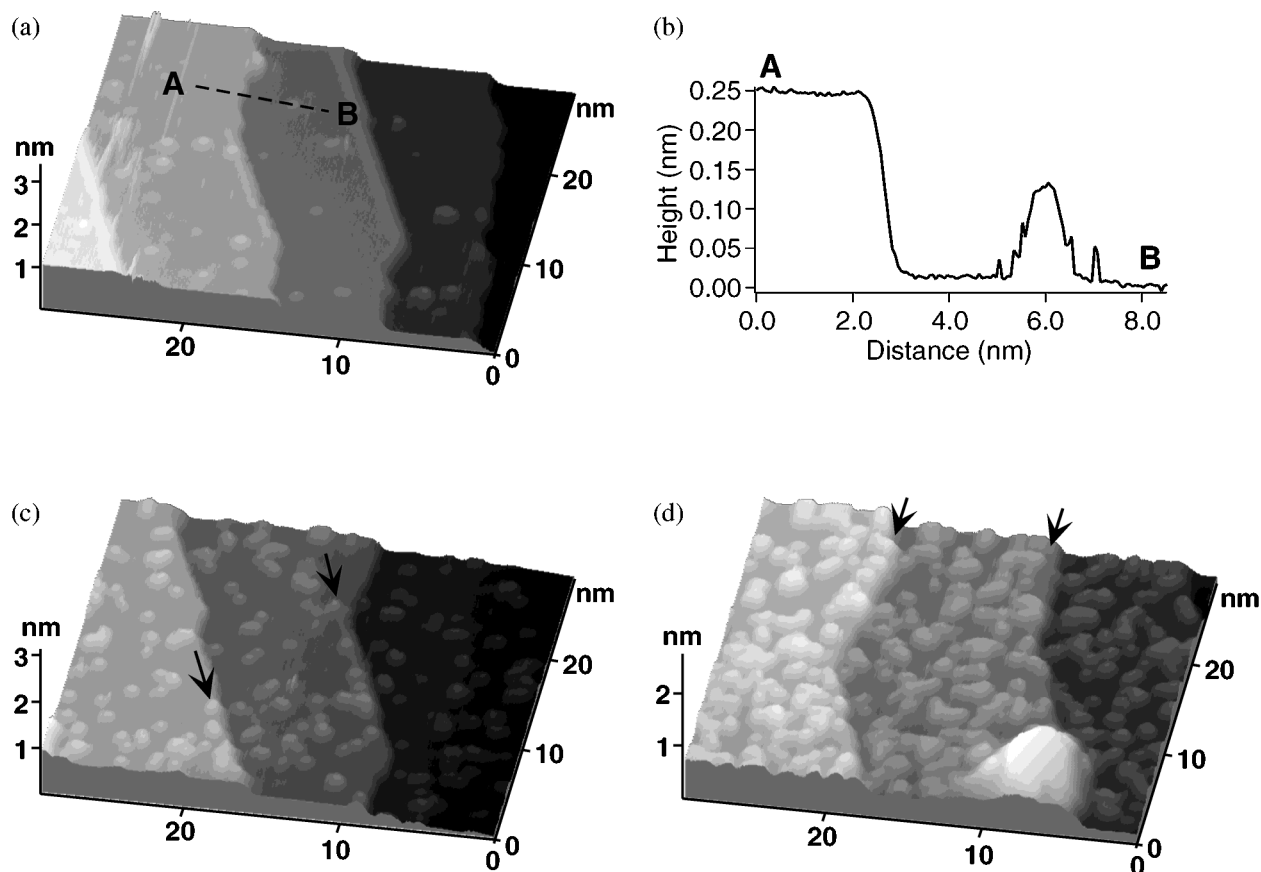


Fig. 1. (a), (c), (d) Series of STM images ($29 \text{ nm} \times 29 \text{ nm}$) taken at 8 K with different Kr coverage (sample bias: $V_s = 0.5 \text{ V}$, tunneling current: $I_t = 0.5 \text{ nA}$). (b) Cross section along A–B in (a).

1(b)). The observed width is large, but each protrusion was resolved even when clusters were formed. In addition, some STM images of the protrusions changed, as indicated by an arrow in Fig. 2(a), during the scan, which can be explained as in the schematic shown in Fig. 2(b); a single Kr atom moved during the scan under the influence of the STM tip. Therefore, we attributed the protrusions in Fig. 1(a) to the single Kr atoms. No preferential adsorption at step edges was observed contrary to the cases of Xe/Pt(111) and Xe/Cu(111).

With additional exposure, adsorption at step edges appeared, with a slight preference for the upper step edges as indicated by arrows in Figs. 1(c) and 1(d). Therefore, the upper step edge does not act as a repulsive barrier against Kr atoms. In addition, as shown in Figs. 1(c) and 1(d), successive adsorption on the upper step edges near the Kr atoms was observed, which indicates that the Kr atoms at the upper step edges do not have repulsive interaction with the Kr atoms which follow. On the basis of the analyses of the diffraction method, annealing at $\sim 25 \text{ K}$ is considered necessary to form well-ordered Kr structures on Pt(111). The observed size of each Kr island is small, as shown in Fig. 1, indicating the short diffusion length of Kr on the Pt(111) surface at this temperature.

Then, the sample temperature was raised to 45 K. Figure 3 shows a typical STM image taken at 45 K for Kr/Pt(111). There exist larger islands of hexagonal shape on the terraces. In addition, as shown in Fig. 3, the step edges are wetted by Kr atoms. In particular, the lower step edge side is completely wetted and the shape of the wetting region is not irregular but

striped; the edge of the wetting region is straight and parallel to the step. A remarkable feature is that the observed height of the Kr images decreased and showed two values, namely, Kr stripes grown from lower step edges were observed to have 0.10 nm height, 0.02 nm higher than those of height 0.08 nm grown on terraces or upper step edges (Fig. 3(b)).

In order to examine the details more closely, the sample was further annealed, and a typical STM image is shown in Fig. 4. Here, the surface is more deeply wetted, and the straight shape of the wetting layer edge is more clearly evident. The wetting regions grown at the upper and lower step edges, are indicated by arrows with the characters U and L, respectively. The shape is extremely straight and the width is greater on the lower step edge side. In addition, there still exist hexagonal islands on the terraces, and in some areas, they bridge the wetting regions at the upper and lower step edges on the same terraces. However, as shown in the cross section (Fig. 4(b)), the height difference remains between the Kr islands on the terraces and the Kr stripes grown from the lower step edges, and a domain boundary exists between them. On the basis of the macroscopic analyses, it is thought that the existence of the step has influence on the growth mode of Kr on the Pt(111) surface, and that this causes the discrepancies between theory and experiments.⁶⁾ The observed difference may be attributed to the difference between the two structures, but further experiments with higher resolution are necessary to clarify this point.

Next, the observed wetting process of the Pt(111) surface by Kr atoms is compared with the characteristics of the

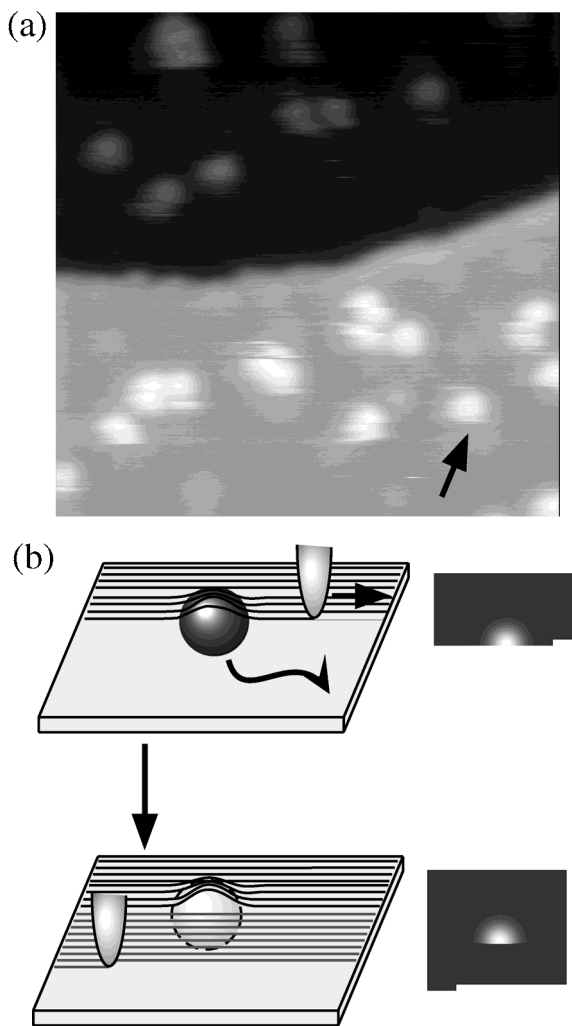


Fig. 2. (a) STM image of Kr/Pt(111) at 6 K ($V_s = 0.5$ V, $I_t = 0.5$ nA, 14.5 nm \times 14.5 nm). (b) Schematic model for the STM image of the protrusion indicated by an arrow in (a).

Xe/Pt(111) and Xe/Cu(111) cases. In both cases of the initial adsorption of Xe/Pt(111) and Xe/Cu(111) at ~ 10 K, the first adsorption of Xe atoms at the upper or lower step edge modifies the electronic structures of the steps, and the Xe atoms which follow start to wet the other side of the step edge. From the observation at 8 K, it is evident that Kr atoms prefer to adsorb at the upper step edges rather than at the lower step edge, similar to the case of Xe/Pt(111). However, contrary to the case of Xe/Pt(111), Kr atoms on the upper step edges do not induce repulsive interaction with the Kr atoms which follow, and do not attract Kr atoms to the lower step edges. Considering these facts, Kr atoms appear to modify the electronic structure of the step edges less than Xe. This difference may be related to the fact that Xe atoms have a stronger dipole moment.

Even at 45 K, the obtained results for Kr/Pt(111) were quite different from those for Xe/Pt(111) and Xe/Cu(111). With annealing at ~ 40 K, in the case of Xe/Pt(111), Xe islands grow larger on the terraces, but the wetting of the step edges occurs only at the lower step edge. The monoatomic chain on the upper step edge remains repulsive even at temperature as high as 40 K. On the other hand, in the case of Xe/Cu(111), the upper step edges are wetted from the beginning at 10 K, and

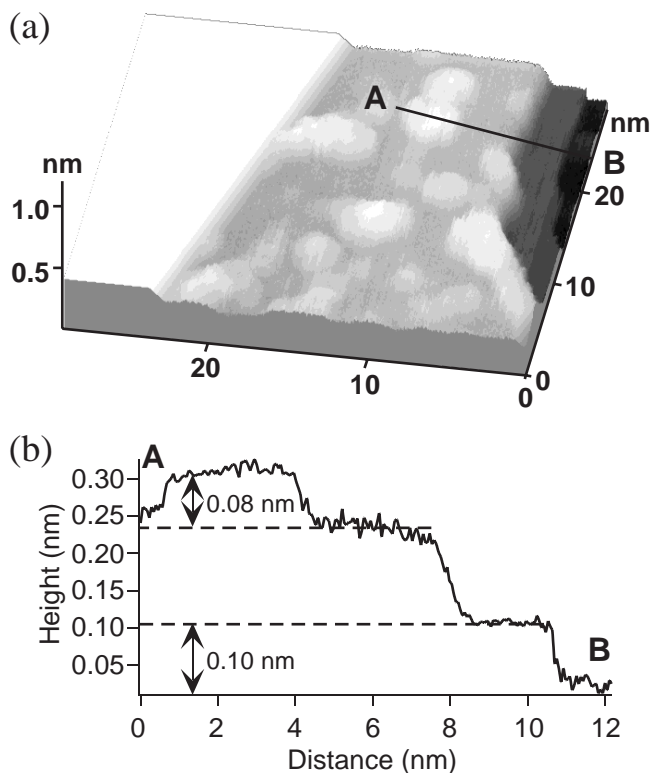


Fig. 3. (a) STM image of Kr/Pt(111) surface taken after annealing at 45 K. ($V_s = 0.5$ V, $I_t = 0.5$ nA, 29 nm \times 29 nm). (b) Cross section along A-B in (a).

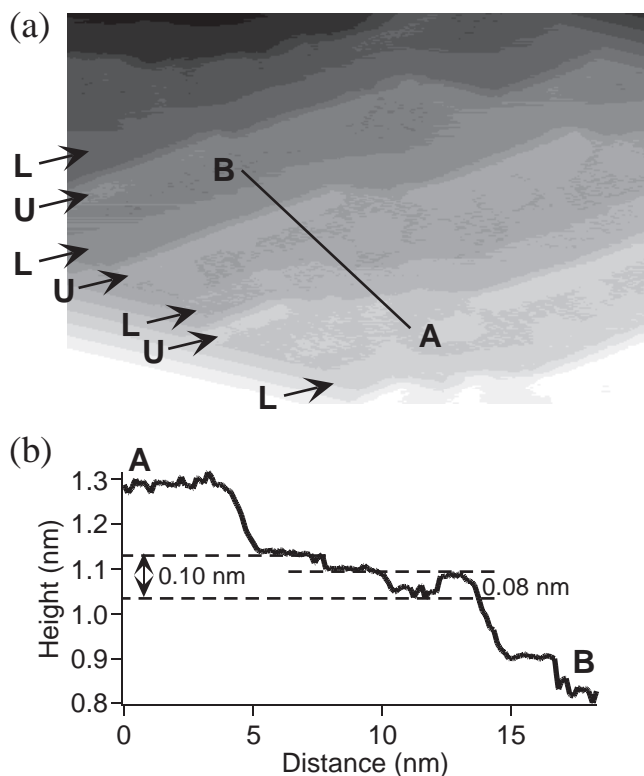


Fig. 4. (a) STM image of Kr/Pt(111) after further annealing of the sample shown in Fig. 3 at 45 K. ($V_s = 0.5$ V, $I_t = 0.5$ nA, 45 nm \times 30 nm). Arrows with the characters U and L indicate the wetting layer at the upper and lower step edges. (b) Cross section along A-B in (a).

the lower step edges become wet as the temperature is raised. Since Kr islands grow both on the upper and lower step edges, the observed wetting process at 45 K appears to be more similar to the case of Xe/Cu(111) than that of Xe/Pt(111), although it differs on several details. Namely, the wetting region on both step edges, particularly on the lower step edge side, grew with a stripe shape, contrary to the irregular structure observed for the cases of Xe/Pt(111) and Xe/Cu(111). In particular, in the case of Xe/Pt(111), the observed structure of the wetting region is very irregular and is considered to have a curly shape.⁹⁻¹²⁾ The result suggests that the interaction between Kr atoms is weaker than in the case of Xe atoms; Kr atoms are adsorbed at the high coordination sites, which makes the edges of the islands straight. This is in good agreement with the observed result at 8 K; Kr atoms do not form islands as described above.

As has been discussed, the observed wetting process of Kr/Pt(111) showed a different characteristic properties from those of Xe/Pt(111) and Xe/Cu(111). Since interactions between rare gases on metal surfaces are considered to be related to the interactions between the adsorbates and the substrates,¹³⁾ a comparative theoretical calculation for the case of Kr, including the electronic structures of the substrate, is strongly needed to understand the wetting process of the rare gases on metals comprehensively.

4. Conclusions

Adsorption and wetting structures of Kr on Pt(111) were studied using STM for the first time. At 8 K, Kr atoms adsorbed on terraces and preferential adsorption to step edges was not observed. With additional exposure, adsorption at step edges occurred, with a slight preference for the upper step edges. However, no evidence for the characteristic properties, such as repulsive interaction between adsorbates or modification of the electronic structures of the step edges was observed. With the increase in temperature up to 45 K, Kr

atoms on terraces increased in size with hexagonal shape, and wetting of the step edges began. During the wetting process, the lower step edge was more preferential, and the wetting region on both step edges grew with a stripe shape; the edge of the wetting region was not irregular but straight and parallel to the steps. In addition, the height of the Kr images decreased and showed two types, namely, Kr stripes grown from the lower step edges were observed to have 0.10 nm height, 0.02 nm higher than those of 0.08 nm height grown on terraces or upper step edges. The obtained results indicate the existence of two different structures, which may be attributed to the two structures previously obtained by macroscopic analyses.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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