Direct Observations of the (1×2) Surface Reconstruction on the Pt(110) Plane

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(Received 26 August 1985)

The reconstruction of the Pt(110) plane from an ordered (1×1) surface to an ordered (1×2) surface has been directly observed for the first time. The (1×1) surface, produced by field evaporation at 78 K, reconstructed at temperatures above 310 K. Field-ion images show clearly that the reconstructed surface consists of alternate missing rows of atoms. The transition was observed for clusters as small as five atoms, implying that the reconstructed surface is stabilized by short-ranged, atomic interactions.

PACS numbers: 68.20.+t, 61.16.Fk

It is well known from low-energy electron diffraction (LEED) studies that the atomic structure of many single-crystal, metal surfaces differs from the bulk-terminated structure. Because the characterization of these so-called surface reconstructions is essential for the development of realistic surface theories and can be important when one attempts to understand the role of surface structure in various surface chemical reactions, there has been an extensive effort to determine the structure of reconstructed surfaces in exact atomic detail. Despite this effort, the atomic structure of many reconstructed surfaces remains controversial.

A specific surface reconstruction which has received considerable attention over the past several years is the reconstruction of the (110) planes of Pt, Ir, and Au.[1-9] The (110) plane of these fcc materials is a channeled surface consisting of alternate rows and troughs of atoms. The reconstruction is characterized by a (1×2) LEED pattern. The most common structure proposed for the reconstructed surface is a "missing-row" structure, in which every other close-packed $[1\bar{1}0]$ row in the outermost layer is missing. For Au surfaces, this missing-row model is supported by direct transmission-electron-microscope[10] and scanning-tunneling-microscope[11] images. In the case of Pt, however, Bonzel and Ferrer[12] have observed a phase transition between the (1×1) and (1×2) surfaces which they claim is inconsistent with the missing-row model. The inconsistency arises because such a phase transformation requires large mass transfer, i.e., rows of atoms must appear and disappear over an area with a diameter as large as the coherence length of the LEED beam. Their calculations indicate, however, that surface diffusion is insignificant at temperatures where the phase transition occurs ($\sim$310 K). To explain the phase transition, they propose a new model for the (1×2) surface which does not require large mass transfer. In a more recent paper, Campuzano, Lahee, and Jennings[13] argue that discarding the missing-row model is not the only way to resolve the inconsistency. If the phase transition is not order-order, but order-disorder [i.e., the (1×1) LEED pattern is due to the ordered second layer, and the top surface is disordered], large mass transfer is not required. On the basis of this assumption, they propose a plausible mechanism for both the origin of missing rows on the Pt(110) plane and the (1×1)-(1×2) phase transition. The question of the exact nature of the (1×2) reconstruction of the Pt(110) plane is therefore still unresolved.

In this paper field-ion–microscope[14] observations are reported which provide direct evidence that the (110) surface of Pt reconstructs to alternate missing rows of atoms. Atomic-resolution images showing the transition from an ordered (1×1) surface to an ordered (1×2) surface have been obtained for the first time. The (1×1) surface which was produced by low-temperature field evaporation,[14] was found to transform to the reconstructed (1×2) surface at temperatures in the range from 300 to 450 K, depending on the size of the plane. The results confirm the missing-row model and support the arguments of Campuzano, Lahee, and Jennings that the (1×2)-(1×1) phase transition observed in LEED is an order-disorder transition.

The present study was motivated, in part, by our recent studies[15] of the diffusion properties of Pt atoms and Pt clusters on the (311) plane of Pt. The (311) plane is similar to the (110) plane in that it consists of close-packed rows of atoms separated by channels. Single atoms were found to migrate along the channels at temperatures as low as 220 K, but dimers and longer chains of atoms within a channel were stable and immobile up to temperatures of 340 K. It was also found that small circular clusters of atoms would transform to linear chains at temperatures above 370 K, further indicating that chains of atoms within a channel were energetically very favorable. This strong attractive interaction was not observed for atoms migrating in adjacent channels. In fact, within the limited statistics obtained, there was evidence for a repulsive interaction. These results suggested that the reconstruction of the Pt(110) plane to alternate missing rows of atoms could be explained by strong, attractive interactions between atoms within a channel and repulsive interactions between atoms in adjacent channels. These nonmono-

tonic adatom-adatom interactions have been predicted theoretically[16,17] and observed experimentally on other surfaces.[18] The results also suggested that a transformation to missing rows of atoms could be observed by field-ion microscopy.

The experimental apparatus used in this study was an all-metal ultrahigh-vacuum field-ion microscope. The background pressure in the system after extensive vacuum processing was $(4-5)\times10^{-11}$ Torr. The Pt tips were prepared from polycrystalline Pt wire following the electrochemical polishing procedure described in the literature[14] and were mounted on a Pt-wire support loop. The tip surfaces were cleaned by a combination of neon-ion bombardment, thermal annealing, and field evaporation. Sample heating was accomplished by the passing of a current through the Pt support loop, and the temperature was monitored by resistance measurements.[19] Neon, purified by diffusion through a Vycor bulb, was used as the imaging gas. An internal channel plate was used for image intensification, and field-ion images were recorded on Kodak Tri-X film with a 35-mm camera.

The experimental procedure used to observe the reconstruction is illustrated in the series of field-ion images shown in Fig. 1. The (1×1) unreconstructed surface was obtained by field evaporation at 78 K. Figure 1(a) shows a (110) plane approximately 40 Å in diameter. Figure 1(b) shows the same surface after the sample was heated to 450 K for 1 min. To avoid any influence by the electric field, the imaging voltage was turned off while the sample was heated. The image shown in Fig. 1(b) indicates that significant surface atom rearrangement has occurred. Moreover, the edge atoms surrounding the (110) plane suggest that the periodicity of rows on the (110) plane has changed. The interior atoms of the (110) plane, which are not imaged in Fig. 1(b), can be revealed by field evaporation, which removes atoms from the edge of the plane inward. Images of the interior atoms exposed by this process are shown in Figs. 1(c) and 1(d). Careful analysis of these images indicates that the rows of atoms lie in alternate channels of the underlying plane. Thus the outer surface consists of atoms in alternate rows of the substrate.

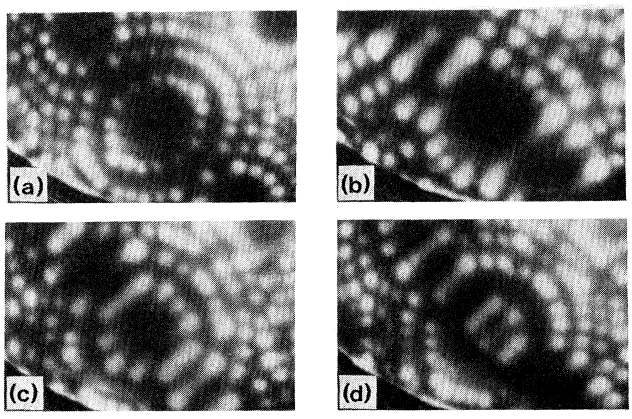

FIG. 1. Series of field-ion images showing the transition of the Pt(110) plane from the (a) field-evaporated (1×1) structure to the (b)–(d) reconstructed (1×2) structure. The reconstruction was produced by the surface being heated to 450 K for 1 min. Images (c) and (d) were recorded after partial field evaporation of the plane and show the missing-row structure.

While the sequence of field-ion images displayed in Fig. 1 clearly shows the transformation from the (1×1) to the (1×2) surface, it could be argued that the process of field evaporation, which was used to reveal the interior atoms, in some way influenced the formation of missing rows. To counter this argument, I have carried out additional experiments with smaller planes of atoms for which field evaporation was not required to see the missing-row structure. Examples are shown in Figs. 2 and 3. Figure 2(a) shows an image of a field-evaporated (110) plane consisting of five rows of atoms. Figure 2(b) shows the same surface after a 1-min heating interval at 330 K. Without any field evaporation, the missing-row structure is evident. Another example is shown in Fig. 3. In Fig. 3(a) the (110) plane has been field evaporated such that just five atoms remain on the plane. Heating the surface to 315 K for 1 min caused the atoms to rearrange to the structure shown in Fig. 3(b). Even for this small number of atoms, the missing-row structure is formed. The atomic transformations shown in Figs. 2 and 3 were reproduced a number of times. In ten experiments, field-evaporated surfaces consisting of four to six rows of atoms in neighboring channels [as in Fig. 2(a)] reconstructed every time to surfaces with two or three rows of atoms in alternate channels [as in Fig.

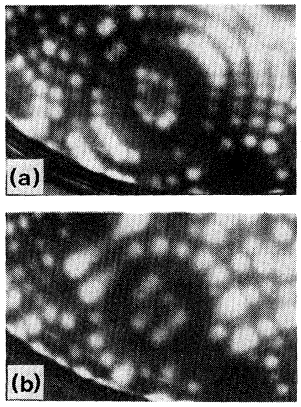

FIG. 2. (a) Field-ion image of a field-evaporated (110) plane consisting of five rows of atoms. (b) The same surface after heating to 330 K for 1 min. The top layer of atoms has rearranged to form alternate missing rows.

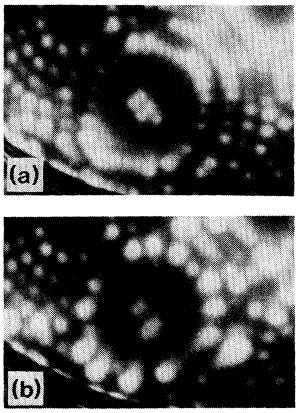

FIG. 3. (a) Field-ion image of a field-evaporated (110) plane with just five atoms remaining on the top surface. (b) The same surface after heating to 315 K for 1 min. A missing-row structure is formed for even this small number of atoms.

2(b)]. In six experiments, short chains of atoms within two or three neighboring channels [as in Fig. 3(a)] transformed three times into a single chain and three times into two chains with a missing row [as in Fig. 3(b)]. The observation of the reconstruction for as few as five atoms on the plane lead us to deduce that the missing-row structure is stabilized by short-ranged atomic interactions, i.e., strong attractive interactions between atoms along the rows and repulsive interactions between atoms in adjacent channels.

The field-ion images shown in Figs. 2(b) and 3(b) indicate that, in addition to the restructuring of the top surface layer, the heating has also caused some rearrangement at the edges of the second (110) layer. It is important to note that this rearrangement was confined to the edges of the plane. Subsequent field evaporation of these edge atoms (which also removed the top layer atoms) confirmed that the surface underlying the missing-row structures was unreconstructed. To avoid perturbation of the underlying layer during heating, experiments are now being carried out with randomly deposited atoms from an external source which migrate at temperatures lower than those required to induce the reconstructuring of small planes of atoms.

It should be mentioned that there have been two previous field-ion microscope studies[20,21] addressing the surface reconstruction of the Ir(110) plane with results contradictory to those reported here. In an investigation primarily devoted to identifying the mechanism for cross-channel diffusion of W atoms on the Ir(110) plane, Wrigley and Ehrlich[20] deduced from the overall size and number of rows on a field-evaporated Ir(110) plane that the distance from one row to the next is roughly twice as large as in the bulk. From this observation they suggested that the *field-evaporated* (110) plane has the same (1×2) reconstructed surface as macroscopic surfaces observed in LEED. In the study reported here, however, it was found that the Pt(110) surface produced by low-temperature field evaporation was unreconstructed. This identification was based on observations of very small (110) planes for which rows of atoms could be seen in each trough of the underlying plane. Only when the surface was heated did we observe the missing rows. No attempt to transform the field-evaporated Ir(110) plane was reported by Wrigley and Ehrlich. On the basis of the present observations, I suggest that the field evaporated (110) plane of Ir is also unreconstructed and that the observations of Wrigley and Ehrlich are perhaps due to the nonuniform magnetification of the field-ion microscope in the region of the (110) plane. Image distortion is a well-known effect in field-ion microscopy,[14] and although the distortion required to infer a (1×2) structure is larger than normally encountered, it could explain the discrepancy. Such nonuniform magnification in no way affects the present conclusions, which are based on direct observations of atoms transforming from chains in every trough to chains in every other trough; nor does it detract from Wrigley and Ehrlich's elegant demonstration that the cross-channel diffusion process proceeds by an exchange mechanism.

Another study relating to the reconstruction of Ir(110) was reported by Adams and Graham.[21] An Ir(110) plane, produced by low-temperature field evaporation, was further field evaporated at temperatures above 300 K. Subsequent field-ion images showed missing rows similar to those reported here. It is important to note that this transformation was induced by field evaporation, not thermal reconstruction as in the work reported here. From this field-evaporation behavior, they concluded that the (110) surface of Ir is buckled, i.e., alternate rows of atoms are elevated leading to preferential field evaporation. No attempt to induce a reconstruction under field-free conditions was reported. In contrast, the present study of the Pt(110) has shown that the reconstruction does indeed take place in the absence of an electric field and that the reconstructed surface consists of missing rows.

In summary, I have shown that an unreconstructed Pt(110) plane produced by field evaporation at 78 K rearranges to an ordered missing-row structure at temperatures in the range from 300 to 450 K. That this rearrangement process has been observed for as few as five atoms on a (110) plane strongly suggests that the (1×2) reconstruction observed on macroscopic surfaces is driven by short-ranged atomic interactions. Although it is not possible to observe the atomic structure of the surface above 300 K by field-ion microscopy (the image contrast is severely reduced at elevated temperatures), the reconstructuring of the surface

deduced from before and after low-temperature field-ion images proves that surface atoms are mobile above room temperature and supports the arguments of Campuzano, Lahee, and Jennings[13] that the (1×1)-(1×2) phase transition observed on macroscopic surfaces is an order-disorder transition, i.e., the (1×1) pattern arises from the unreconstructed second layer, and the topmost layer is disordered at temperatures above ~ 300 K.

The author acknowledges the technical assistance of L. M. Karkiewicz during this project. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

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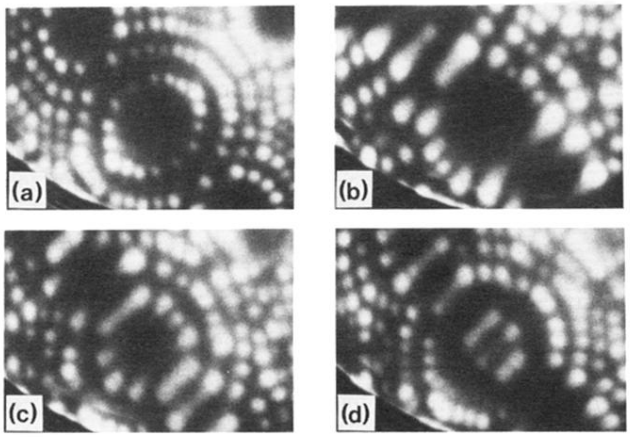

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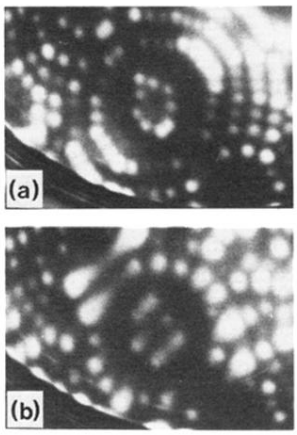

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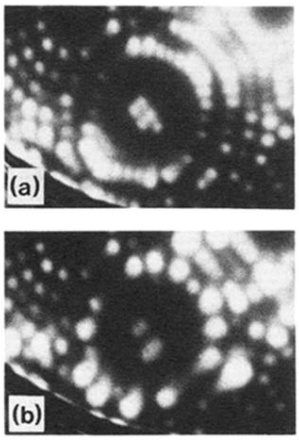

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