PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 MAY 1993-I

Scanning-tunneling-microscopy study of the oxygen-induced reconstruction of Rh(110)

P. W. Murray, F. M. Leibsle, Y. Li,* Q. Guo,* M. Bowker,* and G. Thornton†
Interdisciplinary Research Centre in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom

V. R. Dhanak,‡ K. C. Prince, and R. Rosei§
Sincrotrone Trieste, Padriciano 99, 34012 Trieste, Italy

(Received 18 November 1992)

Scanning-tunneling microscopy has been used to investigate the oxygen-induced $c(2\times2n)$ ($n=3$, 4, and 5) structures on Rh(110). The results show that oxygen induces a $(1\times n)$ reconstruction of the Rh substrate with every nth close-packed row along the $[1\bar{1}0]$ direction missing. This is in contrast to other oxygen-induced reconstructions of face-centered-cubic (110) surfaces where [001] rows are missing, and implies a different driving mechanism for the present case. On the basis of the images and the symmetry of the diffraction patterns, structural models are proposed.

It is well known that the (110) surfaces of most fcc transition metals show a strong tendency to reconstruct, either spontaneously in the cases of Au, Pt, and Ir, or in the presence of adsorbates for metals such as Pd, Ag, Cu, and Ni.[1–12] For example, oxygen adsorption on the (110) surfaces of Cu, Ni, and Ag leads to a reconstruction with added metal-oxygen-metal atoms in the [001] direction, which form $(n\times1)$ structures.[7,11,12] Recently, it has been reported that most oxygen-induced structures on Pd(110) and Rh(110) involve a reconstruction of the substrate, and that this reconstruction is preserved after removal of the oxygen by reduction in hydrogen.[13,14] In particular for oxygen on Rh(110), a variety of surface structures have been reported, depending on the coverage and temperature of treatment.[14–19] Adsorption followed by annealing to 700 K results in $(2\times3)pg$, $(2\times2)p2mg$, and $c(2\times2n)$ structures ($n=3$, 4, and 5) for coverages of 0.25, 0.5, and 0.6 $-$1 ML (monolayer), respectively, with the $c(2\times10)$ structure appearing at the highest coverage. Reduction by hydrogen at 370 K results, respectively, in (1×3), (1×2), and $(1\times n)$ structures which are metastable and revert to (1×1) at temperatures above 480 K.[14] These studies showed that oxygen induces a $(1\times n)$ reconstruction of the rhodium substrate which contrasts with the oxygen-induced $(n\times1)$ reconstructions observed on the (110) surfaces of Cu, Ni, and Ag.

Recent He-diffraction studies of the $(2\times2)p2mg$ structure have shown that the (1×2) reconstruction in this structure is of the "missing-row" type, where every alternate close-packed $[1\bar{1}0]$ row is missing.[20] In the present work, we cannot distinguish between a "missing row" and an "added row," since both appear equivalent under the static equilibrium conditions of the experiment. In order to satisfy the $(2\times2)p2mg$ symmetry seen in low-energy electron diffraction (LEED) and He diffraction, the oxygen atoms have been postulated to sit in the threefold-coordinated sites along the missing-row troughs of the (1×2) reconstructed Rh substrate.[18,19] Each oxygen atom has two equivalent sites within the substrate unit cell and they are alternatively occupied, forming a zigzag chain of oxygen atoms along the troughs. The size of the unit cell is doubled in the $[1\bar{1}0]$ direction, and the zigzag structure gives rise to the glide symmetry of the $(2\times2)p2mg$ structure, with a coverage of 0.5 ML.

This paper presents scanning-tunneling-microscopy (STM) results of the $c(2\times2n)$ O-Rh(110) phases. The results indicate a missing-row reconstruction, where every nth row is missing, and allow us to construct a model for the structure of these high-coverage phases. The advantages of STM in this type of investigation have been demonstrated successfully in a number of recent studies, which are reviewed in Ref. 10.

The STM measurements were performed in an Omicron UHV instrument operated at a base pressure of $<10^{-10}$ mbar. The $c(2\times6)$ and $c(2\times8)$ oxygen-induced structures were prepared by exposing the clean Rh(110) sample to 6 and 12 L of oxygen at 570 K, respectively, while observing the LEED pattern. Although the LEED patterns indicated either $c(2\times6)$ or $c(2\times8)$ patterns, STM showed that there were small domains of both as well as the $c(2\times10)$ structure coexisting with the predominant structure (see below). In the present case this turns out to be advantageous, since it allowed us to examine the three phases from the same set of STM images. The LEED patterns were examined before and after imaging in the STM, and remained unchanged during the measurement, indicating the stability of these structures.

Figure 1 shows a 200×200-Å scan image of the same structure, and several features are apparent. Bright bands are resolved in the $[1\bar{1}0]$ direction, forming groups of three rows parallel to $[1\bar{1}0]$, followed by a trough or missing row. The conventional $c(2\times8)$ unit cell consists of two of these repeat units, i.e., there are six atomic rows and two missing rows per unit cell. Similarly, the $c(2\times6)$ structure consists of a sequence of two atomic rows and one missing row. The image in Fig. 1, while dominated by the $c(2\times8)$ structure, also shows defects in the form of a local sequence of two or four rows of atoms, followed by a missing row. These may be regarded as small areas of $c(2\times6)$ and $c(2\times10)$ structure in the $c(2\times8)$ matrix. The very bright protruding patches are contaminants.

The $c(2\times6)$, $c(2\times8)$, and $c(2\times10)$ phases are shown in detail in Fig. 2. There is a slight elongation of the bright protruding spots in the rows in the direction of the

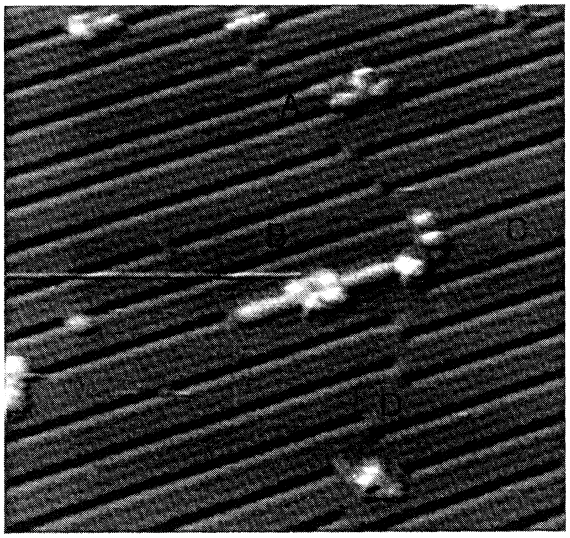

FIG. 1. A 200×200-Å image of the Rh(110) surface after oxygen exposure (12 L, 570 K). The image shows a domain boundary (*D*) between two different reconstructed regions with coexisting phases of (*A*) $c(2\times6)$, (*B*) $c(2\times8)$, and (*C*) $c(2\times10)$ structures ($V=0.35$ V, $I=0.25$ nA).

scan, which is an artifact of the scan conditions. However, it is possible to measure the cell dimensions from constant current profiles taken along the two principal directions of the surface, as shown in Fig. 3. The results indicate that the three structures are very similar except for the distances between missing rows, which depend on the number of rows between the missing rows. An important point to note is that there are always two missing rows in each conventional unit cell, as required by the centered space-group symmetry.

The spacing between adjacent bright rows along the [001] direction is found to be 3.9±0.1 Å, which compares well with the expected value of 3.8 Å. In the $[1\bar{1}0]$ direction along the rows, the maxima in the current profiles are measured to be 5.8±0.2 Å apart, which compares reasonably with the doubling of the lattice spacing in this direction, expected to be 5.4 Å. The discrepancy in the measured values from the expected values is attributed to instrumental factors such as thermal drift and piezoelectric creep.

The corrugation measured along the [001] direction confirms the presence of missing rows of atoms, e.g., for the $c(2\times6)$ structure, we measured a corrugation of 0.7 Å in the missing row compared to 0.16 Å in the protruding rows. This is very similar to the case of the (1×2) missing-row structure of Au(110), where the STM corrugation was found to be 0.8 Å,[21] which provides qualitative support to the interpretation.

Our STM images do not resolve the oxygen site in the reconstructed $c(2\times2n)$ structures. However, the observation of the missing row, and the fact that the removal of oxygen leads to a metastable $(1\times n)$ structure,[14] suggests a possible model for the structures (Fig. 4). We propose a $(1\times n)$ missing-row structure, with oxygen in a zigzag arrangement in the troughs along the $[1\bar{1}0]$ direc-

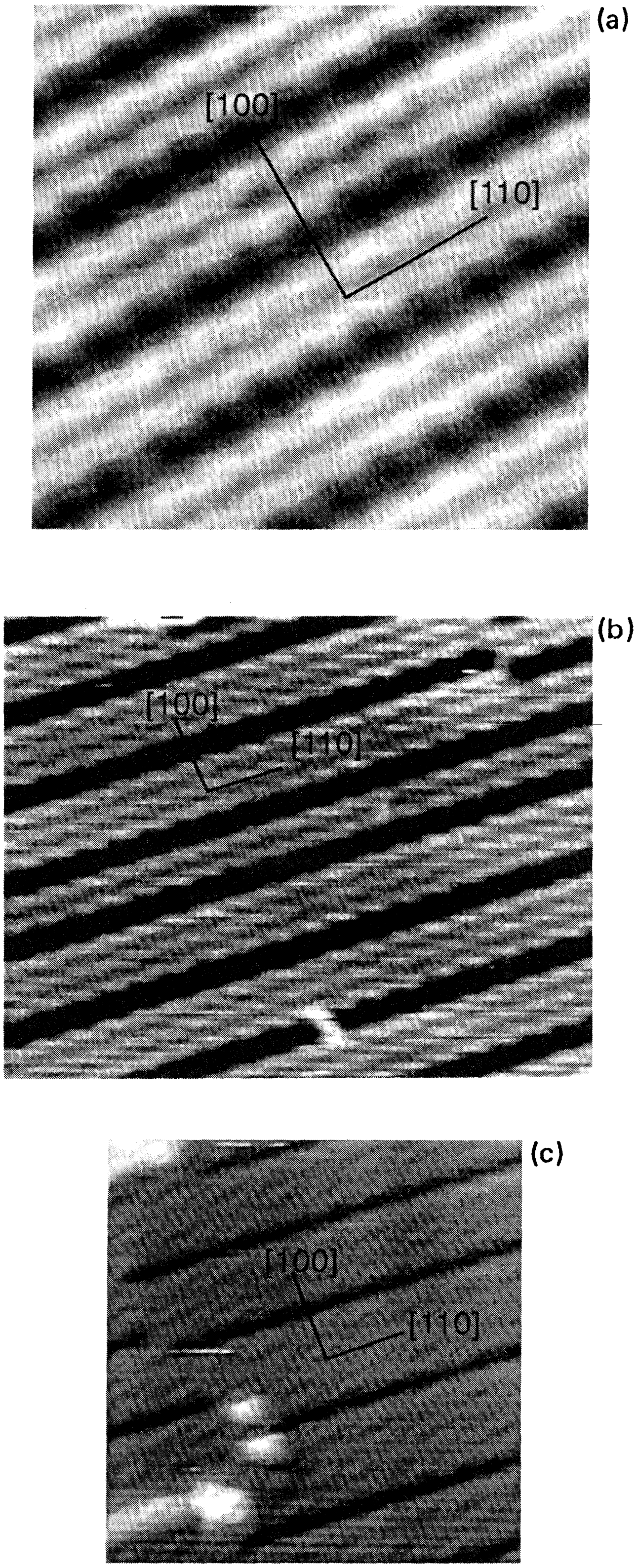

FIG. 2. (a) A 50×50-Å image of the $c(2\times6)$ structure ($V=1.5$ V, $I=1$ nA). (b) A 90×110-Å image of the $c(2\times8)$ structure ($V=0.4$ V, $I=0.25$ nA). (c) 80×80-Å image of the $c(2\times10)$ structure ($V=0.4$ V, $I=0.25$ nA).

tion and occupying a threefold-coordinated site. This model is based on a number of observations concerning the LEED patterns. At low temperature and high coverage, a $(2\times1)p2mg$ structure is formed, in which the oxygen is believed to form zigzag rows in the troughs. At a coverage of 0.5 ML and a temperature sufficient for surface diffusion of rhodium, a $(2\times2)p2mg$ structure forms, in which the oxygen again forms zigzag rows in the troughs. In this case, the substrate is reconstructed to form a (1×2) missing-row structure. For the $c(2\times2n)$ structures, the STM images show that the number of missing rows varies with n, i.e., that one out of every n rows is missing. The model is constructed from these two structural elements, missing Rh rows and zigzag oxygen chains, with the further requirement that the observed space-group structure is present, i.e., centered rather than glide-line structures. It can easily be shown that the centered structures can only be produced by arranging the zigzag rows out of phase; if they are in phase, glide structures are produced. As noted in Ref. 18, the threefold-coordinated site is not unreasonable for oxygen on Rh(110), based on preliminary high-resolution electron-energy-loss spectroscopy (HREELS) data. However, in this model, oxygen in the missing-row troughs sits lower than in the (1×1) troughs. It is also possible that the oxygen in the missing-row troughs may be adsorbed in one of two threefold-coordinated sites of the (111) facets.

The coverages indicated by the model of Fig. 4 are in agreement with the reported coverages[14,16–18] for the $c(2\times2n)$ structures. The coverage can be varied continuously from 0.5 to 1.0 by adjusting the number of missing rows. For a $c(2\times2n)$ structure, the coverage is expected to be $(n-1)/n$. We suggest that at 0.5-ML coverage, the lowest-energy state has oxygen adsorbed in the troughs of missing rows, resulting in the $(2\times2)p2mg$ structure. However, this minimum energy is only a little lower than the unreconstructed state, because the interactions of an oxygen atom with its nearest Rh and O neighbors are similar and only the second nearest neighbors

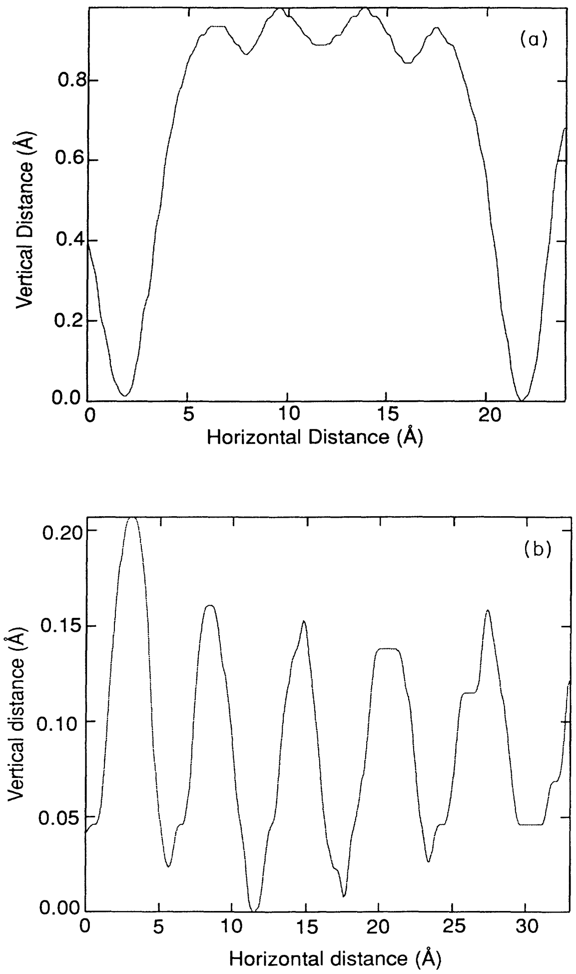

FIG. 3. Typical constant current profile scans along (a) the [001] and (b) [1$\bar{1}$0] directions, measured from the image of the $c(2\times10)$ structure.

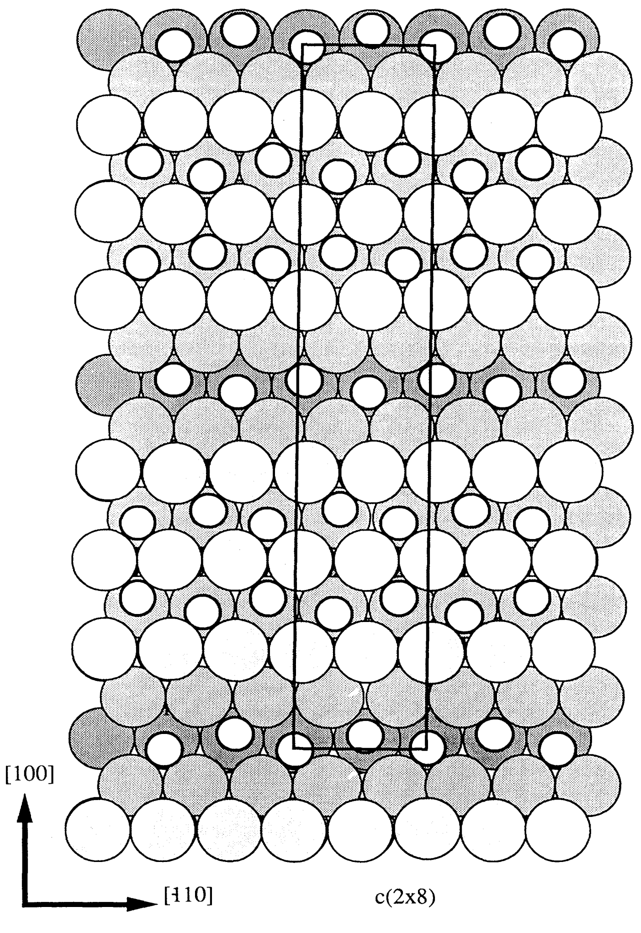

FIG. 4. The missing-row structural model for the $c(2\times8)$ oxygen-induced phase on Rh(110). The large circles are the Rh atoms and the small circles are the oxygen atoms. The $c(2\times6)$ and the $c(2\times10)$ structural models can be constructed in a similar way with every third and fifth row, respectively, of Rh atoms missing in the [1$\bar{1}$0] direction.

are different. As the coverage is increased, more oxygen adsorption sites can be provided if the surface partially reverts to the unreconstructed state, and it does so with a regular array of missing rows, involving long-range oxygen-oxygen interactions over at least half a unit cell in the [001] direction.

The oxygen-induced reconstructions seen on Ag(110), Ni(110), Cu(110), and Cu(100) appear to be driven by the formation of chains of alternating metal and oxygen atoms along the [001] direction.[7,11,12] In contrast, the present reconstruction seems to be driven by the formation of missing-row troughs, allowing the oxygen to be more deeply embedded in the troughs. It is likely that the oxygen-induced reconstruction of Pd(110) is like Rh, as He *et al.*[22] have suggested, since the reconstruction has a (1×2) periodicity. Within the group-VIII and -IB family of metals, it seems that the $[1\bar{1}0]$ missing-row reconstruction is favored going down the Periodic Table and to the left, so that the 5*d* metals are reconstructed even without oxygen. The metals toward the top and right evidently reconstruct in a different way.

The structural model proposed here is intended to indicate only the overall arrangement of the surface atoms, and does not take account of small relaxations of the surface atoms which may occur. Such displacements must be consistent with the space-group symmetry of the surface structure, and could involve relaxations of the Rh atoms on the edges of the troughs away from the troughs, for instance. Indeed there seems to be some evidence for such displacements, as evidenced in the line scan of Fig. 3(a). The rows of atoms adjacent to the missing rows are at a different vertical distance from other rows. This could indicate a relaxation effect, although it may also be caused by the limited lateral resolution of the tip. In addition, preliminary polar-angle x-ray-photoelectron-diffraction results provide evidence of some lateral shifting of the atoms away from their bulk positions.[23]

In summary, we have reported a STM study of the oxygen-induced reconstruction of Rh(110). Three phases of the type $c(2\times2n)$ ($n=3$, 4, and 5) have been imaged. The results show that the associated substrate reconstruction is of the $(1\times n)$ type with missing rows, in contrast to that seen on Cu, Ni, and Ag. Structural models are proposed involving oxygen in a zigzag arrangement along the troughs.

This work was supported by the United Kingdom Science and Engineering Research Council.

---

[*] Also at: Leverhulme Centre for Innovative Catalysis, University of Liverpool, Liverpool L69 3BX, UK.

[†] Also at: Department of Chemistry, University of Manchester, Manchester M13 9PL, UK.

[‡] Also at: INFM-TASC, Padriciano 99, 34012 Trieste, Italy.

[§] Also at: Dipartimento di Fisica, Universitá di Trieste, 34000 Trieste, Italy.

[1] M. Garofalo, E. Tosatti, and F. Ercolessi, Surf. Sci. **188**, 321 (1987).

[2] S. P. Chen and A. F. Voter, Surf. Sci. **244**, L107 (1991), and references therein.

[3] G. A. Somorjai and M. A. Van Hove, Prog. Surf. Sci. **90**, 201 (1989).

[4] B. E. Hayden, K. C. Prince, P. J. Davie, G. Paolucci, and A. M. Bradshaw, Solid State Commun. **48**, 325 (1983).

[5] R. J. Behm, in *Physics and Chemistry of Alkali Metal Adsorption,* edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).

[6] A. M. Baro, G. Binnig, H. Rohrer, Ch. Gerber, E. Stoll, A. Baratoff, and F. Salvan, Phys. Rev. Lett. **52**, 1304 (1984).

[7] D. J. Coulman, J. Wintterlin, R. J. Behm, and G. Ertl, Phys. Rev. Lett. **64**, 1761 (1990), and references therein.

[8] Y. Kuk, P. J. Silverman, and H. Q. Nguyen, Phys. Rev. Lett. **59**, 1452 (1987).

[9] R. Raval, S. Hag, M. A. Harrison, G. Blyholder, and D. A. King, Chem. Phys. Lett. **167**, 391 (1990); see also P. Hu, L. Morales de la Garza, R. Raval, and D. A. King, Surf. Sci. **249**, 1 (1991).

[10] J. Wintterlin and R. J. Behm, in *Scanning Tunneling Microscopy I,* edited by H.-J. Guntherodt and R. Wiesendanger, Springer Series in Surface Sciences Vol. 20 (Springer, New York, 1992), p. 39 and references therein.

[11] I. Stensgaard, L. Ruan, F. Besenbacher, F. Jensen, and E. Laegsgaard, Surf. Sci. **269/270**, 81 (1992), and references therein.

[12] T. Hashizume, M. Taniguchi, K. Motai, H. Lu, K. Tanaka, and T. Sakurai, Jpn. J. Appl. Phys. **30**, L1529 (1991).

[13] V. R. Dhanak, G. Comelli, G. Paolucci, K. C. Prince, and R. Rosei, Surf. Sci. Lett. **260**, L24 (1992).

[14] V. R. Dhanak, G. Comelli, G. Cautero, G. Paolucci, K. C. Prince, M. Kiskinova, and R. Rosei, Chem. Phys. Lett. **188**, 237 (1992).

[15] C. W. Tucker, Jr., J. Appl. Phys. **37**, 4147 (1966), and corrections in **38**, 2696 (1967).

[16] E. Schwarz, H. Lenz, H. Wohlgemuth, and K. Christmann, Vacuum **41**, 167 (1990).

[17] M. Bowker, Q. Guo, and R. Joyner, Surf. Sci. **253**, 33 (1991).

[18] G. Comelli, V. R. Dhanak, M. Kiskinova, G. Paolucci, K. C. Prince, and R. Rosei, Surf. Sci. **269/270**, 360 (1992).

[19] G. Comelli, V. R. Dhanak, M. Kiskinova, N. Pangher, G. Paolucci, K. C. Prince, and R. Rosei, Surf. Sci. **260**, 7 (1992).

[20] A. F. Bellman, D. Cvetko, A. Morgante, M. Polli, F. Tommasini, V. R. Dhanak, A. Lausi, K. C. Prince, and R. Rosei (unpublished).

[21] J. K. Gimzewski, R. Berndt, and R. R. Schlittler, Phys. Rev. B **45**, 6844 (1992).

[22] J. W. He, U. Memmert, K. Griffiths, and P. R. Norton, J. Chem. Phys. **90**, 5082 (1989).

[23] M. Bowker, S. M. Francis, and M. Newton (unpublished).

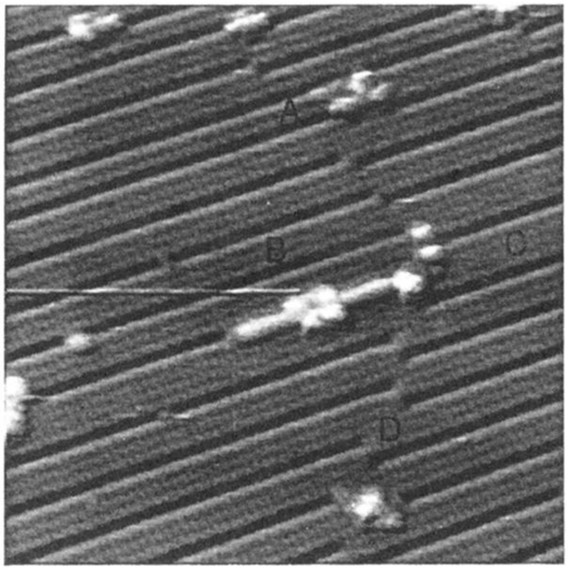

FIG. 1. A 200×200-Å image of the Rh(110) surface after oxygen exposure (12 L, 570 K). The image shows a domain boundary (*D*) between two different reconstructed regions with coexisting phases of (*A*) $c(2\times6)$, (*B*) $c(2\times8)$, and (*C*) $c(2\times10)$ structures ($V=0.35$ V, $I=0.25$ nA).

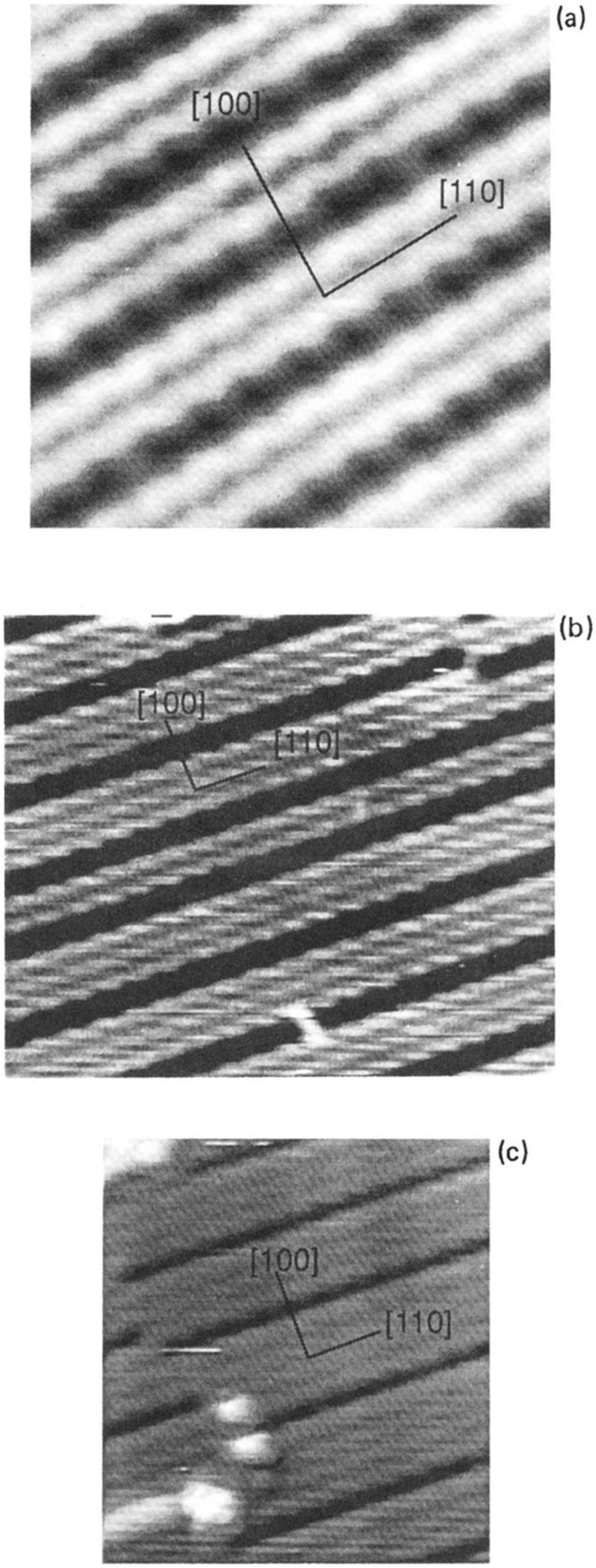

FIG. 2. (a) A 50×50-Å image of the $c(2\times6)$ structure ($V=1.5$ V, $I=1$ nA). (b) A 90×110-Å image of the $c(2\times8)$ structure ($V=0.4$ V, $I=0.25$ nA). (c) 80×80-Å image of the $c(2\times10)$ structure ($V=0.4$ V, $I=0.25$ nA).