Mechanism of the CO-Induced $1\times 2 \rightarrow 1\times 1$ Structural Transformation of Pt(110)

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Direct observation of the removal of the "missing row" reconstruction of the clean Pt(110) surface under the influence of CO adsorption by scanning tunneling microscopy revealed that at 300 K this process is initiated by homogeneous nucleation of small characteristic 1×1 patches. Their further growth is limited by thermal activation; migration of Pt atoms is restricted to a few lattice sites. At higher temperatures, correlated jumps cause the lateral displacement of longer chains, and the enhanced surface mobility leads to the formation of larger, strongly anisotropic 1×1 islands.

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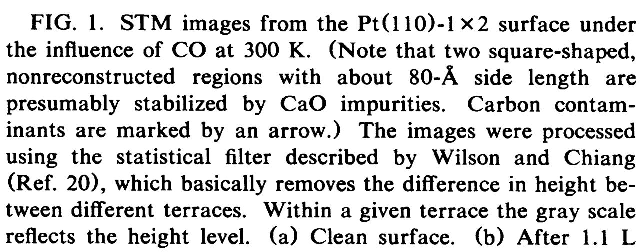
Many surfaces undergo structural transformations under the influence of an adsorbate.[1] The microscopic mechanisms of these processes are still widely unknown, in particular, in those cases which are associated with substantial changes of atomic density in the topmost layer. The lifting of the 1×2 reconstruction of the Pt(110) surface by adsorption of CO[2-5] represents a prototype for these systems. The clean Pt(110) surface exhibits a structure in which every second row in the $[1\bar{1}0]$ direction is missing,[6,7] and hence, production of the nonreconstructed 1×1 phase involves a 100% increase in atomic density. The adsorbate-induced disappearance of the half-order LEED spots, which are characteristic of the 1×2 phase, has been observed to take place even at 250 K.[4] This temperature, on the other hand, is far too low to permit surface diffusion of Pt atoms over longer distances.[8] The so-called sawtooth model for the 1×2-phase[4] offers a solution to this dilemma, since it would require only atomic jumps over one lattice constant, but it can clearly be ruled out as the correct structure.[6,7] Alternatively, the disappearance of the 1×2-long-range order was proposed to be the consequence of an order-disorder transition,[9] which would again only involve small diffusion steps. So far, however, any direct experimental evidence has been missing. In this Letter we will report on observations, by means of high-resolution scanning tunneling microscopy (STM), of this surface structural transformation which reveal directly atomic-scale information about the mechanism of this process. This mechanism, which involves migration of Pt atoms over very short distances only, is not of the order-disorder type, but leads to the formation of 1×1 domains, albeit associated with an appreciable degree of (kinetically limited) disorder.

The experiments were performed under ultrahigh-vacuum (UHV) conditions using a pocket-size STM with a mechanically driven tip-sample approach.[10] The principle of preparation of tungsten tips yielding high resolution has been described elsewhere.[11] In short, the tip was brought into a high-resolution state by briefly raising the tunnel voltage to -9 V while tunneling on a Au(110) surface, which was then replaced by the actual Pt(110) sample. STM images were recorded in the constant-current mode, typically at 50–250-mV potential applied at the sample and a preset tunnel current of 0.5 to 5 nA. Sample preparation using standard recipes[2,3] and surface analysis by LEED and Auger-electron spectroscopy (AES) were performed *in situ*. The level of surface contaminants was reduced to below 1% as judged by AES. After final annealing to 1000 K LEED exhibited a 1×2 pattern with slightly elongated extra spots on a rather low background, reflecting the formation of a well-ordered reconstructed surface with an estimated average terrace width in the [001] direction of below 100 Å, while the width in the $[1\bar{1}0]$ direction was larger and exceeded the transfer width of the LEED instrument.

This conclusion is confirmed by the STM images from the clean surface, for which a typical example is reproduced in Fig. 1(a). The terraces, elongated in the $[1\bar{1}0]$ direction, exhibit a one-dimensional corrugation of the same type as previously reported for the 1×2-Au(110)



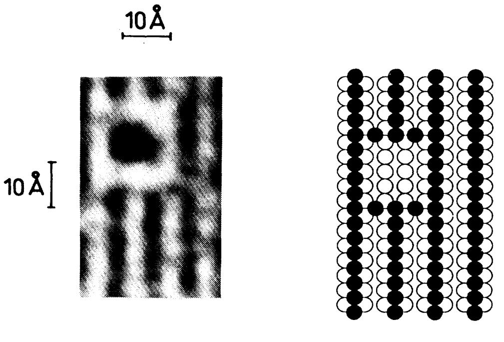
(a) (b) (c)

FIG. 1. STM images from the Pt(110)-1×2 surface under the influence of CO at 300 K. (Note that two square-shaped, nonreconstructed regions with about 80-Å side length are presumably stabilized by CaO impurities. Carbon contaminants are marked by an arrow.) The images were processed using the statistical filter described by Wilson and Chiang (Ref. 20), which basically removes the difference in height between different terraces. Within a given terrace the gray scale reflects the height level. (a) Clean surface. (b) After 1.1 L CO exposure. (c) After 1.5 L CO exposure.

surface.[12] The separation of 7.9 ± 0.2 Å between adjacent rows is equal to twice the lattice constant in the [001] direction (=7.84 Å), and hence the rows in the STM image can be identified with atomically close-packed [1$\bar{1}$0] rows forming the "missing row" 1×2 reconstruction. The corrugation amplitude varied between 0.3 and 0.6 Å, depending on the experimental parameters and tip conditions. The qualitative features of the images were, however, found not be be affected by the tunneling parameters such as bias voltage or current. Residual carbonaceous surface impurities (as identified by AES) are resolved in the STM images [arrow in Fig. 1(a)].

Exposure of the clean 1×2 surface to CO at temperatures between 300 and 450 K caused gradual disappearance of the half-order LEED spots, i.e., removal of the long-range order of the reconstruction, in accordance with reports in the literature.[2-5] More specifically, at room temperature this process has been found to require a critical CO coverage $\theta_{\mathrm{CO}}\approx 0.2$ (corresponding to an exposure of about 1 L, whereby 1 L$=0.75\times10^{-4}$ Pa s) for nucleation.[5] A series of STM images, taken at 300 K, as reproduced in Fig. 1 demonstrates the type of structural changes that are observed by this technique. It should be noted that under the applied conditions the adsorbate remains always "invisible," so that only structural features of the substrate are displayed. Again the 1×2 surface is stable up to an exposure of 0.8 L. After 1.1 L exposure the image [Fig. 1(b)] exhibits features which may be described as small holes surrounded by a ring of atoms. These holes are randomly distributed over the terraces without any preference for defects, while the overall step-terrace topography is preserved. This indicates the occurrence of a homogeneous nucleation process. At 300 K, further CO exposure leads to an increase of the density of these holes, rather than to growth of the already existing ones, while other parts of the surface still exhibit the 1×2 reconstruction [Fig. 1(c)]. This increase of the density of holes continues with increasing exposure up to about 3 L. Then the lifting of the reconstruction is completed and patches with 1×2 periodicity are no longer discernible. The resulting structure, if investigated by more integral techniques such as LEED[6] or medium-energy ion scattering (MEIS),[7] would exhibit a high degree of disorder in the form of steps, while the present observations show that atomic-scale *local* order still exists.

Inspection of magnified STM images [Fig. 2(a)] provides information about the kinds of atomic displacements connected with this process: Within a "hole" the close-packed [1$\bar{1}$0] row of Pt atoms is interrupted on a length of the order 10–15 Å. These atoms were obviously shifted only over short distances to missing-row sites as depicted schematically in Fig. 2(b). In this way the holes are formed, whose bottom as well as ridges consist of elements of the nonreconstructed 1×1 phase. The difference in height between the bottom and ridge of the holes is about twice the 1×2 corrugation (0.7–1.0 Å) which can be reconciled, within the limits of accuracy, with the spacing between adjacent (110) planes of Pt. (The measured depth is reduced by the limited resolution of the STM.) Typically about four to six atoms are removed from a [1$\bar{1}$0] row within a hole, leading to a local 1×1 patch with dimensions of the order of 10×10 Å^2.



(a) (b)

FIG. 2. (a) Magnified image of one of the "holes" and (b) corresponding ball model.

These results demonstrate that the CO-induced structural transformation is not simply an order-disorder transition within the topmost layer leading to a random configuration of the Pt atoms.[9] Furthermore, it does not proceed through correlated, i.e., simultaneous, lateral displacements of [1$\bar{1}$0] strings, as proposed recently for the reverse process, the 1×1→1×2 transformation of the clean surface, on the basis of field-ion-microscope (FIM) observations.[13,14] Instead, local 1×1 nuclei are created which require atomic motion only over two to three lattice sites.

At 300 K, the formation of the 1×1 nuclei actually proceeds considerably slower than the adsorption of CO. After finishing a CO exposure, i.e., after the coverage has reached a constant value, the density of 1×1 patches was observed to still increase by up to 20% over a period of several minutes. This qualitative finding indicates that under these conditions the structural transformation is decoupled from the adsorption process.

The phenomenology is quite different at elevated temperatures. Figure 3(a) shows an STM image recorded at 350 K after about 1.2 L CO exposure. Now, longer [1$\bar{1}$0] strings are apparently shifted in the [001] direction by one lattice constant, as becomes evident from inspection of the encircled area and sketched schematically in Fig. 3(b). Nucleation at defect sites such as the termination of atomic strings on a terrace plays a significant role. Also the quasicorrelated motion of neighboring atoms as well as diffusion along the troughs becomes feasible. This leads to the formation of larger (but strongly anisotropic) domains of the 1×1 phase.

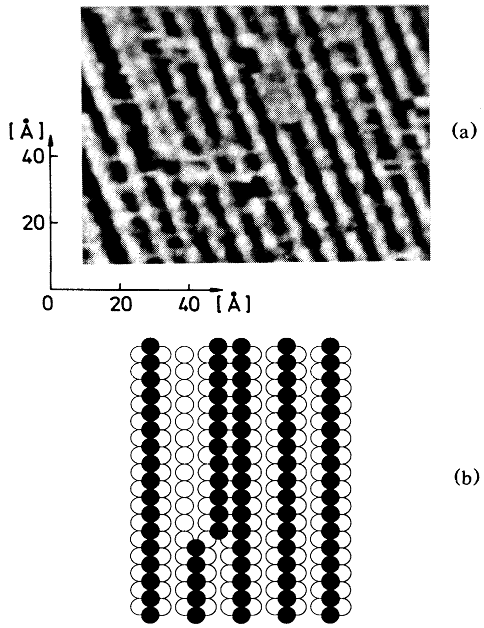


FIG. 3. (a) STM image recorded at 350 K showing partial $1\times2\rightarrow1\times1$ transformation by parallel displacement of pieces of $[1\bar{1}0]$ rows and (b) corresponding ball model.

After reaching saturation of the adlayer the surface consisted of 1×1 patches with typical dimensions of 20-50 Å in the [001] direction and 100–300 Å in the $[1\bar{1}0]$ direction.

These observations, which on a first view are quite contrasting, can be rationalized in terms of a common picture for the microscopic mechanism of the adsorbate-induced structural transformation of the 1×2-Pt(110) surface: At an (overall) coverage of around 0.2 the *local* concentration of adsorbed CO, as reached by statistical density fluctuations within the adlayer, may become high enough to render the 1×1 phase energetically more favorable. At room temperature homogeneous nucleation of the type depicted in Fig. 2(b) may take place through the jump of a single Pt atom by one lattice spacing in the [001] direction. This nucleation step is activated. At $T<250$ K it is almost completely inhibited,[3,4] and even at 300 K it takes several minutes to reach the new equilibrium after establishing a fixed CO coverage. In FIM experiments on the surface self-diffusion of individual adatoms on Pt(110), jumps to neighboring sites were found to proceed at 290 K on the time scale of 1 min with similar probabilities in both the $[1\bar{1}0]$ and [001] directions and with activation energies of around 18 kcal/mol.[8] The energy for the thermal formation of an adatom on a perfect Pt(110) surface was, on the other hand, estimated to be of the order of 23 kcal/mol.[15] However, the disrupture of the $[1\bar{1}0]$ rows will be assisted by the presence of the CO adsorbate so that this energy will be reduced. If combined with "normal" preexponentials this will yield time scales of the observed order of magnitude, which seem to be generally characteristic for adsorbate-induced structural transformations of fcc(110) transition-metal surfaces,[16] quite in contrast, e.g., to the hex→ 1×1 transformation of Pt(100) which proceeds even at 150 K.[17]

Next, the displaced atom migrates along the trough until it is "trapped." At 300 K, the attractive interaction with *two* neighboring atoms [cf. Fig. 2(b)] is presumably strong enough to prevent further diffusion. The Pt atoms terminating the interrupted $[1\bar{1}0]$ row in turn are destabilized and migrate subsequently to similar sites with two neighbors. This process proceeds "atom after atom;" that means a migrating Pt atom is trapped before the next one is displaced, thus leading to formation of the holes as the predominant topographic feature. Further growth ceases at this point, and instead new nuclei are created upon further CO adsorption.

At 350 K, on the other hand, the jump of a Pt atom out of a $[1\bar{1}0]$ row by one lattice constant in the [001] direction can be followed by another atom before the first one has migrated away to a trap site. Additional attractions between nearest neighbors in $[1\bar{1}0]$ will favor the displacement of the second atom into the same direction, leading to correlated, albeit not simultaneous, motion of the type observed in a FIM study of the reverse process, viz., $1\times1\rightarrow1\times2$.[14] As a consequence longer chains are displaced. Their termination occurs if the local CO coverage drops below the critical value. Heterogeneous nucleation at terrace edges plays a more dominant role: The probability for homogeneous nucleation will be smaller, since due to the increased mobility of the adsorbed CO molecules the lifetime of critical clusters of CO_{ad} will be reduced. At defect sites presumably fewer CO molecules will be needed to initiate the transformation. Second, nuclei at terrace edges can grow appreciably to domains which finally cover a significant fraction of the surface area, whereas at 300 K their effect is restricted to the terrace edges themselves. Also, 1×1 patches nucleated within a terrace can readily grow towards the boundary of this terrace and will then be indistinguishable from those nucleated at the edges. The anisotropic shapes of the 1×1 domains result from coalescence of few displaced $[1\bar{1}0]$ rows. At even higher temperatures the enhanced mobility of the Pt atoms gives rise to the formation of larger 1×1 domains at the expense of dissolution of smaller islands (Ostwald ripening).

The "nucleation and growth" mechanism derived for the present system is of the same type as that proposed previously for the CO-induced lifting of the "hex" reconstruction of Pt(100),[18] for which system again small metastable 1×1 domains are created that grow to larger domains at elevated temperatures.[19]

In summary, direct imaging by means of the STM enabled us to demonstrate how an adsorbate-induced structural transformation of a surface can proceed without the need for long-range displacement of surface atoms, even if their actual *local* density changes by a factor of 2. The microscopic mechanism consists of two steps, nucleation through adsorbate-induced, activated breakup of the initial atomic configuration followed by surface diffusion and trapping which leads, depending on temperature, to characteristic shapes and size distributions of the domains from the new phase.

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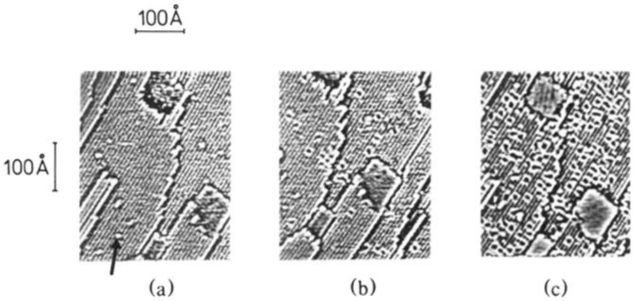
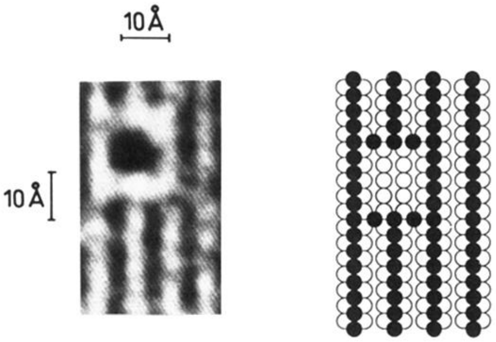


(a) (b) (c)

FIG. 1. STM images from the Pt(110)-1 × 2 surface under the influence of CO at 300 K. (Note that two square-shaped, nonreconstructed regions with about 80-Å side length are presumably stabilized by CaO impurities. Carbon contaminants are marked by an arrow.) The images were processed using the statistical filter described by Wilson and Chiang (Ref. 20), which basically removes the difference in height between different terraces. Within a given terrace the gray scale reflects the height level. (a) Clean surface. (b) After 1.1 L CO exposure. (c) After 1.5 L CO exposure.



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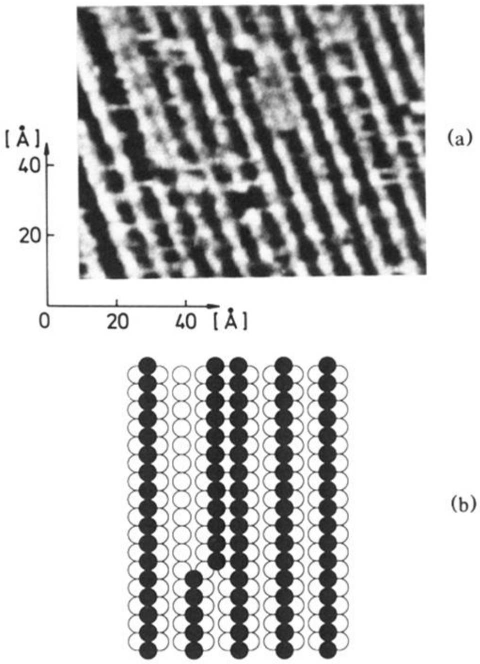

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