Role of Surface Elastic Relaxations in an O-Induced Nanopattern on Pt(110)-(1 × 2)

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Scanning tunneling microscopy shows that a nanopattern forms as the Pt(110)-(1 × 2) surface is exposed to oxygen at room temperature or above. The nanopattern consists of $[1\bar{1}0]$ oriented O-induced stripes assembling into a (11 × 2) superstructure at high O coverage. The stripes form because the O adsorption energy increases by expanding the Pt lattice along the ridges of the surface as compared to the bulk. From interplay with density functional theory calculations, we show that the O-induced nanoscale periodicity is caused by short-ranged elastic relaxations confined to the surface.

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The self-assembly of nanoscale patterns on surfaces has been observed in a variety of systems, e.g., [1–6]. To control these structures it is necessary to understand the mechanisms that govern their stability. One commonly proposed model attributes pattern formation to the relief of surface stress allowed by elastic relaxations into the bulk [7,8]. Although this model has explained pattern formation in some cases, it was recently emphasized by Ozoliņš *et al.* [9] that this continuum bulk model may not provide a satisfactory description at the nanometer scale, because relaxations confined to the surface become of increased importance.

In this Letter, we examine the mechanisms governing nanopatterns formed by O adsorption on Pt(110)-(1 × 2). Scanning tunneling microscopy (STM) reveals that O adsorbs in $[1\bar{1}0]$ oriented stripes. These stripes in turn self-assemble into [001] oriented ribbons that lead to the formation of a periodic and anisotropic nanostructure. We combine density functional theory (DFT) calculations with STM observations of the elastic relaxations and thermal fluctuations of the patterns to probe the energetics governing this structure. We find that the relaxation of surface stress does indeed account for the observed patterns. However, the stress relief occurs through lattice relaxations mainly confined to Pt ridges on the Pt(110) surface with bulk relaxations playing little role.

The experiments are performed in a UHV chamber equipped with the variable-temperature Aarhus STM [10]. The O-induced patterns form when the clean Pt(110)-(1 × 2) surface is exposed to O_2 at pressures in the range of 1×10^{-8} to 5×10^{-7} mbar and at temperatures at or above room temperature (RT) [11]. Under such conditions, O_2 adsorbs dissociatively on the surface [12], and the Pt(110)-(1 × 2) reconstruction remains intact [13].

To monitor the formation of the O patterns, STM movies were acquired during O exposure. Figure 1 shows images from such a movie [14]. Initially, the Pt $[1\bar{1}0]$ ridges appear noisy due to mobile O atoms, Fig. 1(a). After an exposure of ∼10 L, bright stripes on the ridges protrude an additional ∼0.4 Å. These stripes were assigned to PtO_2 units involving ridge-Pt atoms and a local 1.0 ML of O bound in fcc sites on the (111) nanofacets of the ridges [11,15]. At a stripe coverage above ∼0.04 ML stripes on adjacent Pt ridges tend to align along the [001] direction, Figs. 1(b)–1(d). This alignment causes the buildup of bright ribbons perpendicular to the Pt ridges. The formation of the 2D nanopattern appears to be an equilibrium phenomenon because thermal fluctuations are abundant; movies as

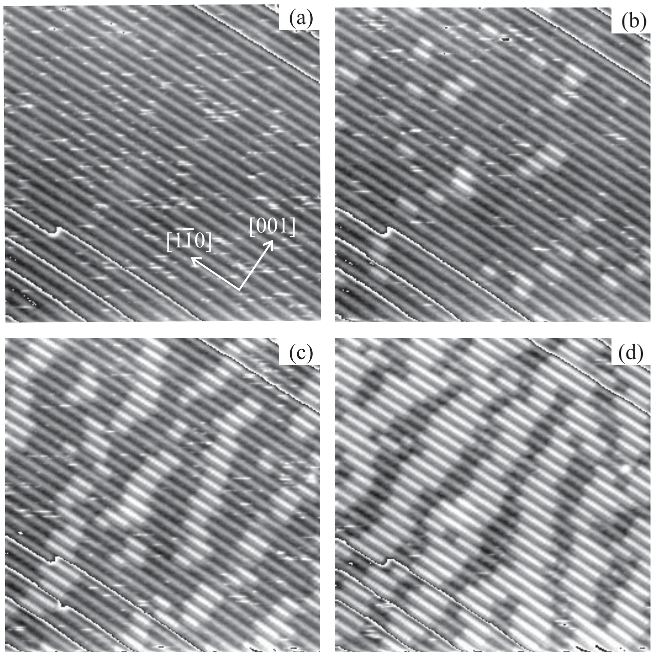

FIG. 1. Stills from an STM movie show the formation of an O-induced pattern at $T = 357$ K [14]. The full gray scale is applied to each terrace, so steps appear as white/black lines in the $[1\bar{1}0]$ direction. The O dosage is (a) 10 L, (b) 18 L, (c) 39 L, and (d) 205 L. Image size 208 × 226 Å^2. $I_t = 1.10$ nA and $V_t = -10.4$ mV. Frame rate = 0.12 sec^{-1}.

Fig. 1 show that about 70% of the stripes are displaced in the $[1\bar{1}0]$ direction between consecutive images.

To measure the equilibrium properties of the nanopatterns, we exposed the surface to oxygen at several temperatures above 400 K and subsequently imaged the static surface at RT. The average stripe length l and the periodicity d along the Pt ridges were determined as a function of stripe coverage (Fig. 2). l increases from $\sim 3.5a_{[1\bar{1}0]}$ to $\sim 5.4a_{[1\bar{1}0]}$ with increasing coverage (the $[1\bar{1}0]$ lattice constant $a_{[1\bar{1}0]} = 2.78$ Å). At a stripe coverage of ~0.5 ML, d is $\sim 11a_{[1\bar{1}0]}$, consistent with an observed (11×2) LEED pattern. Figure 2 shows no temperature dependence of l and d suggesting they are determined by energetics. The degree of order in the patterns is probed by the standard deviation of many independent measurements of the d (the error bars in Fig. 2): Only at stripe coverages above ~0.15 ML do the patterns become well-ordered.

First, we address the stripe stabilizing mechanism and ask why the equilibrium configuration consists of O-covered ridges of finite length rather than an extended phase that minimizes the energetic cost of terminating the stripes. According to DFT calculations, the structure of the extended phase with the highest O binding energy consists of a 1.0 ML structure of fully O-covered ridges [11,15]. Such structures are, however, not allowed to relax in the $[1\bar{1}0]$ direction. Using DFT [16], we find considerable surface stresses, 0.295 eV/Å^2 [17] and -0.150 eV/Å^2 in the $[1\bar{1}0]$ direction for the clean and 1.0 ML O-covered ridges, respectively. Since the stresses have opposite signs, the realization of a mixed structure of alternating clean and O-covered regions will allow for stress relief of both regions. This is exactly what happens when the stripes of Fig. 1 form, as shown in the STM image of Fig. 3(a). From a line-scan analysis of the position of the protrusions, corresponding to the ridge-Pt atoms [11], we find the Pt atoms are uniformly separated within the stripes and the length of the stripes is expanded compared to the bare ridge, corresponding to an increase in the Pt lattice constant by ~5%.

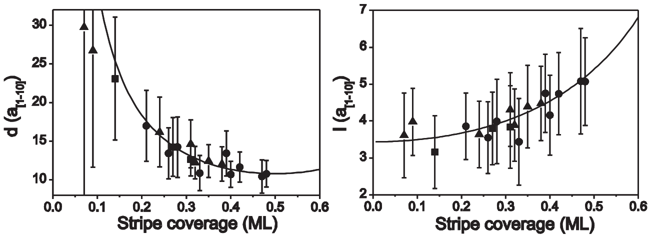

FIG. 2. The stripe periodicity d and length l (in units of $a_{[1\bar{1}0]} = 2.78$ Å) versus stripe coverage. During O_2 exposure the substrate temperature was 400 K (circles), 500 K (triangles), or 600 K (squares). Each data point is the average over 100–200 independent measurements, and the error bars show the corresponding standard deviation. The full curves are the best fit to the bulk stress theory [8].

To investigate whether this stress relaxation is responsible for the energetic stability of the (11×2) phase, we have evaluated the energy gain upon stress relief with DFT. We have considered a 0.55 ML O structure using the (11×2) unit cell containing 12 O atoms [Fig. 3(b)]. Relaxing the top three Pt layers but fixing $[1\bar{1}0]$ coordinates at bulk truncated positions, the adsorption energy (with respect to 1.0 ML O structure) is raised by 31 meV/O, corresponding to a cost of 31 meV × 12 = 0.372 eV to terminate the PtO_2 structure of Fig. 3(b). (With the [110] coordinates fixed as those in the pure phases a slightly higher termination energy of 0.480 eV is obtained.) After releasing the constraints along $[1\bar{1}0]$ the total energy of the (11×2) cell is lowered by 1.256 eV. The overall energy gain with respect to the 1.0 ML O structure is 74 meV/O. Thus,

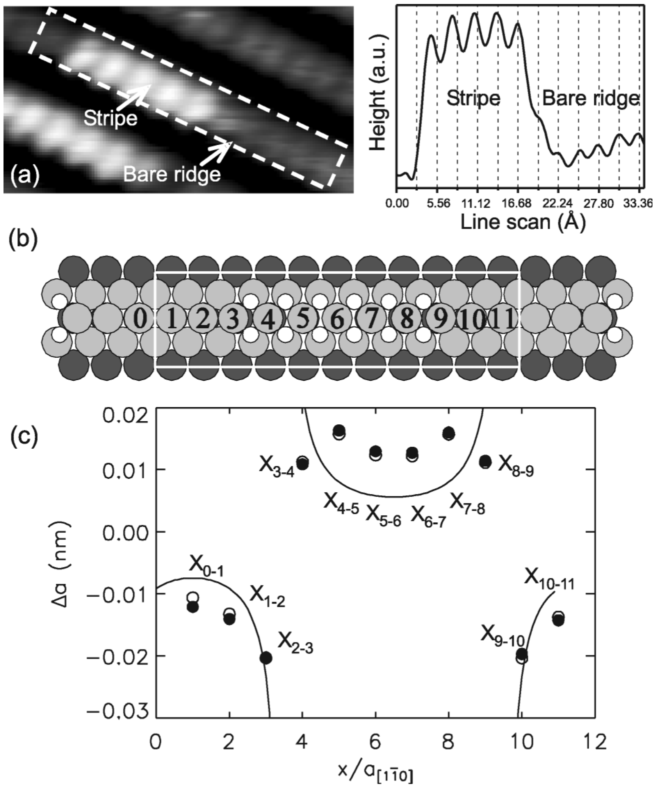

FIG. 3. (a) Atom-resolved STM image of O-induced stripes obtained at 304 K. The line scan along the Pt ridge (dashed rectangle) reveals a uniform Pt-Pt separation within the stripes having an average lattice spacing expanded by 5% compared to the bare ridge (the grid lines denote Pt positions in the latter). (b) Ball-model of the (11×2) O-induced nanostructure on Pt(110)-(1×2). A Pt ridge (light gray) with adjacent (111) facets (darker gray) are shown with O atoms (white) adsorbed in fcc sites. The ridge-Pt atoms in the dense O domains are imaged as brighter stripes with STM [11]. (c) The solid (open) circles show the calculated relaxations of the $[1\bar{1}0]$ spacing of the ridge-Pt atoms labeled in (b) using DFT with the third Pt layer relaxed (fixed). The solid line gives the relaxations expected from Eq. (1).

the observed elastic relaxation in the $[1\bar{1}0]$ direction is indeed responsible for the stability of the stripe structure.

Next, we discuss the spatial extent of the elastic relaxations. In Fig. 3(c) we present the relaxations along $[1\bar{1}0]$ calculated with DFT. The total expansion of the stripe (~1 Å) is reasonably consistent with STM. Relaxations calculated with three (closed circles) and two (open circles) Pt layers relaxed are found to be very similar, suggesting that the stress relief does not require bulk relaxations. This result is significant because in the theory of Marchenko [7] for pattern formation bulk relaxations mediate the relief of surface stress and bulk elastic constants determine the size and energy of the relaxations. Allowing only for relaxation of the top two Pt layers (and the O atoms), the energy gain for structure in Fig. 3(b) with respect to the 1.0 ML O structure is 65 meV/O. Being only 9 meV smaller than the result for three relaxed Pt layers, this result suggests that the stripe stabilizing stress relief occurs primarily on the surface and is independent of bulk relaxations. Further confirmation of this conclusion is obtained by comparing the size of the relaxations with those allowed by bulk relaxations. From Marchenko's isotropic bulk elasticity theory of stress relaxation, the variation $\Delta a(x)$ in spacing between Pt atoms along the ridge is [7]

$$\frac{\Delta a(x)}{a_{[1\,\bar{1}\,0]}} = \frac{1-\nu^2}{Ed}\Delta\sigma\cos\left(\frac{p\pi}{2}\right)\csc\left(\frac{\pi x}{d}\right)\sec\left(\frac{p\pi}{2}+\frac{\pi x}{d}\right), \tag{1}$$

where p is the ratio of the difference in the area between the clean and O-covered regions to the total area, $\Delta\sigma$ is the difference in surface stress, ν and E are Poisson's ratio and Young's modulus of the substrate, respectively. The solid line in Fig. 3(c) shows the variation in spacing between Pt atoms along the ridge according to Eq. (1), with the stress mismatch taken from DFT and using the Pt elastic constants needed to generalize Marchenko's theory to an elastic anisotropic substrate [18]. Compared to Marchenko's model, the DFT spacing in the O-covered ridge is significantly larger and more uniform. Indeed, the uniform relaxation within the ridge, consistent with experiment, suggests that the coupling to the substrate is small compared to the repulsion between Pt atoms in the O-covered ridge.

We now consider the interactions that cause the stripes to form the 2D nanopattern. The development of the stripe period (Fig. 2) is caused by repulsive interactions between stripes in the $[1\bar{1}0]$ direction. In the extreme case, elastic displacements completely limited to the surface generate exponentially [9] decaying repulsive interactions between stripes of considerably shorter range than the $1/r^2$ interactions [8,19] due to bulk relaxations. A question is therefore whether the surface-constrained interactions are strong enough to account for the O-induced periodicity. To address this issue we estimate the strength of the stripe-stripe interactions along the $[1\bar{1}0]$ ridges from the thermal distribution of stripe separations by applying the procedure developed to probe the interactions between surface steps. If the meandering of the ribbons is characterized by the mean square displacement b^2 between the centers of neighboring stripes in the [001] direction, and $U(x)$ is the interaction energy per unit length between stripes separated by x (along $[1\bar{1}0]$), then the root-mean-square of the $[1\bar{1}0]$ separation between the stripes, w, is given by [20]

$$w = \left(\frac{k_B T b^2}{8U''(\langle d\rangle)a_{[001]}}\right)^{1/4} \tag{2}$$

where $\langle d\rangle$ is the average separation between the centers of stripes and $a_{[001]}$ is the [001] lattice constant. For a stripe coverage of 0.47 ML formed at 400 K and imaged at RT, we find that $w \approx 1.0a_{[1\bar{1}0]}$, $b^2 \approx 2.0a_{[1\bar{1}0]}$, and $\langle d\rangle \approx 11a_{[1\bar{1}0]}$. Substitution of these values into Eq. (2) then gives

$$U''(d = 11a_{[1\bar{1}0]}, l = 5a_{[1\bar{1}0]}) = \frac{15\text{ meV}}{a^2_{[1\bar{1}0]}a_{[001]}}. \tag{3}$$

Patterns formed at the other temperatures give similar values (Fig. 2). From Marchenko's theory [using the same elastic constants as in Eq. (1)] we find that this interaction is only 4 meV$/(a^2_{[1\bar{1}0]}a_{[001]})$. So to determine if the observed large size of this interaction is consistent with interactions due to the displacement of Pt atoms constrained to the ridges, we estimated U'' with DFT in the following way. We constructed three different (12×2) unit cells with two stripes, each with three pairs of O atoms on one Pt ridge (Fig. 4). In the first unit cell [Fig. 4(a)], the centers of the O stripes are separated by $6a_{[1\bar{1}0]}$, in the second [Fig. 4(b)] by 7 and 5 $a_{[1\bar{1}0]}$, and in the third [Fig. 4(c)] by 8 and 4 $a_{[1\bar{1}0]}$. If the top three layers are allowed to relax, the O adsorption energy difference in DFT between the first and second and the first and third of these configurations is 24 and 156 meV, respectively. These energy differences are related to U'' by $[U(d-\varepsilon) + U(d+\varepsilon) - 2U(d)]a_{[001]} \approx U''(d)a_{[001]}\varepsilon^2$, where ϵ is either $a_{[1\bar{1}0]}$ or $2a_{[1\bar{1}0]}$. Averaging the estimates of U'' for the two configurations

$$U''(d = 6a_{[1\bar{1}0]}, l = 3a_{[1\bar{1}0]}) = \frac{34\text{ meV}}{a^2_{[1\bar{1}0]}a_{[001]}}. \tag{4}$$

If only the top two layers are allowed to relax, the U'' becomes slightly larger: 43 meV$/a^2_{[1\bar{1}0]}a_{[001]}$, indicating that surface-confined relaxations are primarily responsible for the interaction. The value of U'' in Eq. (4) is approximately twice the number in Eq. (3), measured for larger stripe separations. This increase is expected because of the strong decrease in elastic distortions away from the stripes on the bare ridge seen in Fig. 3. For comparison, Marchenko's theory gives for the configuration in Eq. (4) a much smaller value of 16 meV$/(a^2_{[1\bar{1}0]}a_{[001]})$. From the

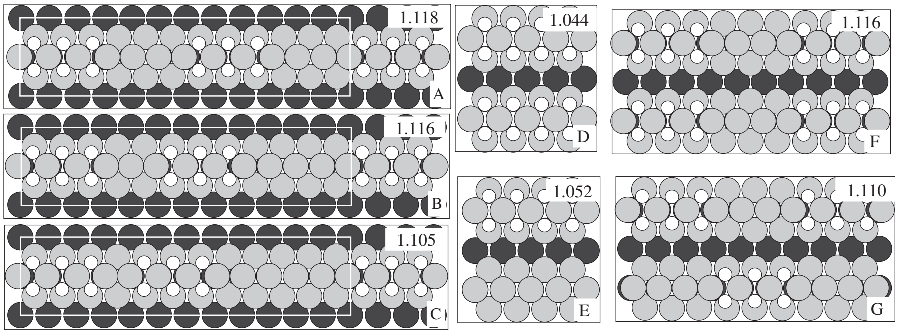

FIG. 4. Atomic configurations used to estimate the interaction energy between stripes. The adsorption energies per O atom with the top three Pt layers and O atoms relaxed are given.

order of magnitude agreement between the theoretical value of the bulk-insensitive U'' and the experimental value, we conclude that elastic relaxations confined to the ridges are sufficient to explain the interactions responsible for the observed nanoscale periodicity.

Finally, we turn to the origin of the formation of ribbons in the [001] directions. The attraction between stripes responsible for the ribbons could be caused by elastic relaxations in the substrate because neighboring O-covered ridges of finite length would both tend to expand the substrate along $[1\bar{1}0]$ in the same way. We tested this idea by performing a DFT calculation of the adsorption energy for a structure in which completely filled (hence without bulk strain fields caused by $[1\bar{1}0]$ relaxations) O-covered ridges alternate with empty ridges [Figs. 4(d) and 4(e)]. By comparing this energy with that for a surface with all ridges covered, a small repulsion of 16 meV per pair of O atoms between stripes is obtained. However, by calculating the O adsorption energy for a (6×4) unit cell in which three pairs of O atoms cover each ridge, either with the O-covered ridges adjacent to each other in the [001] direction or not [Figs. 4(f) and 4(g)], we find an attraction of 12 meV per pair of O atoms. As this attraction was found only when relaxing the top three Pt layers, it suggests that elastic relaxations along $[1\bar{1}0]$ are also responsible for the ribbons by perturbing the deeper bulk layers.

In summary, we have determined that the nanoscale O-induced patterns observed on Pt(110)-(1×2) are caused by elastic relaxations occurring in response to a compressive surface stress of the O-filled Pt(110) surface and a tensile stress of the clean surface. We find that elastic relaxations confined to the Pt ridges are primarily responsible for the stress relief. This finding is in striking contrast to the importance of bulk relaxations found in other systems [21,22] and is caused by the fact that the coupling between elastic relaxations in the Pt ridges and the bulk are relatively weak.

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