Correlation between Domain Boundaries and Surface Steps: A Scanning-Tunneling-Microscopy Study on Reconstructed Pt(100)

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(Received 1 July 1985)

From results of a scanning-tunneling-microscopy study we show that, on Pt(100), (i) boundaries between different rotational domains of the hexagonal reconstruction only occur at steps and (ii) neither the step direction nor (iii) the orientation of the respective neighbored domain dictates the direction of the reconstructed domain. The domain-domain and domain-step interactions decrease in the same order; their magnitude and the activation energy for reorientation of domains is related to a structural transition of this surface at 1100 K.

PACS numbers: 61.55.Fe, 61.70.Ng, 61.70.Yq

Surface structures of lower symmetry than the corresponding bulk lattice in general are realized in several domains, e.g., rotational or translational domains. The domain boundaries are assumed to represent local maxima in the potential energy on surfaces as well as in bulk systems.[1] We report here experimental evidence from scanning tunneling microscopy[2] that on well annealed surfaces the system avoids this energetically unfavorable situation in a simple way: Boundaries between domains with different rotational orientation occur only at surface steps where the rise in potential energy is minimal. This effect was observed on the hexagonally reconstructed Pt(100) surface which exhibits four different rotational domains.

The Pt(100) surface is well known to undergo an irreversible reconstruction at $T > 420$ K.[3,4] Its LEED pattern is reported to exhibit extra spots of a 5×25 or "hexagonal" structure and upon annealing to $T > 1100$ K of a "rotated hexagonal" structure. The corresponding real-space structures have been interpreted in terms of a hexagonal layer of topmost atoms which is rotated by 4.6° with respect to the substrate[5-7] leading to four possible rotational domains.

The experiments were performed with a scanning tunneling microscope based on similar concepts to the one developed by Binnig *et al.*,[2] which is described in more detail elsewhere.[8] It contained facilities for sample cleaning (Ar^+-ion bombardment) and characterization (LEED, Auger-electron spectroscopy) and for indirect heating of the sample. The tunneling current ($I_t \approx 5$ nA) was measured at the tip with the tunneling voltage ($V_t = 0.01-0.8$ V) applied to the sample. The calibration of the piezoelectric drives was based on the measured height of well defined steps on the surface. The sample was cleaned by our following standard procedures[9] until no contaminations were detectable by Auger-electron spectroscopy (AES) ($< 1\%$). After being annealed to 1100 K the surface exhibited the LEED pattern of the rotated hexagonal reconstruction as it is described in the literature.[5,6] The measurements were performed mostly at 500 K to inhibit adsorption from the residual gas ($p \approx 1\times10^{-10}$ Torr) and to reduce the time span necessary to reach sufficient thermal stability.

The clean Pt(100) surface typically consists of large flat domains of several hundred angstroms diameter. They are separated mostly by monatomic and biatomic steps. Macroscopic imperfections and insufficient annealing temperatures following ion bombardment always lead to considerably decreased terrace sizes. Intended chemical contamination detectable by AES (e.g., carbon, $> 1\%$) results in microscopically rough structures without resolvable terrace formation.

In high-sensitivity scans of the flat parts of the surface a corrugation was detected which is characteristic of the hexagonal reconstruction of the surface and results from the mismatch between the (1×1) substrate and the hexagonal topmost layer.[8] The lateral extension of the strictly periodic corrugation becomes evident from Fig. 1 in which two scans over a large area are displayed. Both of these scans exhibit constant corrugation amplitudes of ~ 0.4 Å and corrugation lengths of ~ 14 Å over their entire range of ~ 2000 Å. [The deviations from a linear base line are due to a slight distortion effect ($< 0.1\%$) in that particular piezoelectric drive system and to nonlinearities in the thermal drift.] While in one of the scans the surface is completely flat (except for the corrugation), in the other one two additional irregular features are detected. They can be ascribed to small islands of "adsorbed" Pt which are in [100] spacings two layers high. These scans are representative of the surface in-

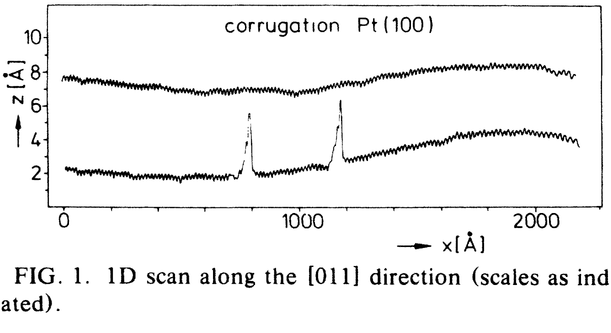

FIG. 1. 1D scan along the [011] direction (scales as indicated).

sofar as we have never detected a change in the corrugation length or amplitude on a single terrace.

Examples involving different terraces are given in Figs. 2 and 3. The three-dimensional model displayed in Fig. 2 represents an array of 2D scans over an area of 500×170 Å.^{2} (The ratio of the scan speeds in the x and y directions was 100:1; only part of the traces was used for the model.) It shows two extended plateaus separated by a monatomic step both of which exhibit the corrugation of the reconstructed surface. While their corrugation amplitudes are again about 0.4 Å, the corrugation length varies considerably from 14 Å in the lower domain to 42 Å in the upper domain. On changing the scan direction we could also verify that the long corrugation is caused by the same corrugated structure which, however, in the latter case is rotated with respect to the scan direction. Further details concerning the correlation between structure and corrugation in both reconstructed structures will be published elsewhere.[8] The difference in corrugation length thus results from different angles between scan direction and corrugation, determined here to be $-5° \pm 5°$ and $+70° \pm 2°$, respectively, which is in good agreement with the LEED pattern. The basic length of the corrugation of 14 Å also corresponds exactly to the fivefold periodicity of the reconstruction.[8] Consequently, the two domains are rotated with respect to each other by $75° \pm 7°$, which is close to the predicted value of about 81°.[5,7] Clearly the step is not parallel to the corrugation of the upper terrace, while on the lower terrace step orientation and corrugation "hills" are aligned reasonably well.

Figure 3(a) shows original recorder traces as measured by the scanning tunneling microscope. Again two terraces are exhibited which are separated by a double step. Also in this case the corrugation lengths differ, although less obviously than in the preceding figure, from 19.5 Å in the upper terrace to 17 Å in the lower terrace. On the assumption of the same basic length as before (14 Å/unit) the two domains are rotated by 46° and 56° with respect to the scan direction. The difference is also evident from the thick lines in Fig. 3(a) which indicate the corrugation directions of the respective terraces. For two domains rotated to either side of the [011] lattice direction, the angular divergence amounts to 9.2°, close to the observed value of 10°. In this case the second lateral dimension was introduced experimentally by thermal drift. Its magnitude and direction could be determined from the angle between the corrugation directions as well as by comparison with the LEED pattern. The area actually scanned is indicated in Fig. 3(b) together with the respective corrugation lengths and directions. As in the first example, the step is not parallel to the corrugation; rather the corrugation hills merge into the step on both terraces.

Both figures directly demonstrate that the reconstruction extends right into the steps, i.e., the steps represent grain boundaries between the reconstructed topmost layer of the lower terrace and the unreconstructed second layer of the upper terrace. As experienced from many other measurements, these figures are representative for the surface in the following aspects: We have seen all possible combinations of domains with different rotational orientation on either side of steps. Monatomic and biatomic steps were observed where the concentration of biatomic steps as compared to the number of single steps was higher than expected from statistics. A variety of different

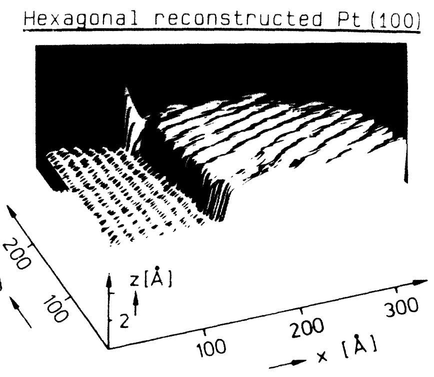

FIG. 2. 3D model of a Pt(100) surface, obtained from a 2D array of scans (scale as indicated).

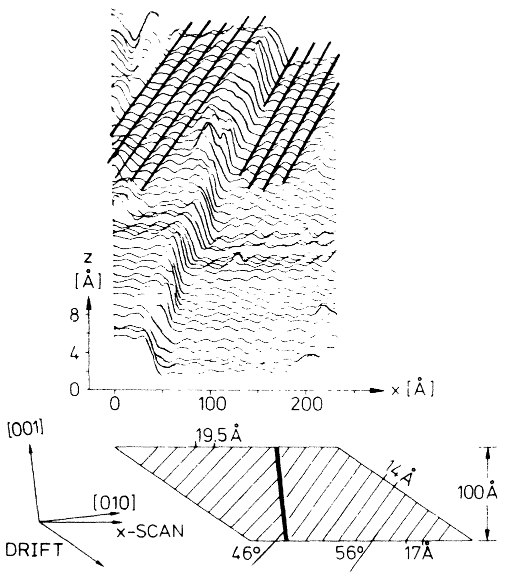

FIG. 3. (a) Recorder traces of 1D scans 6° off from the [010] direction; thick lines represent the direction of corrugation (scales as indicated). (b) Actually scanned surface area (corrugation lengths and directions as well as step directions are indicated).

combinations between steps in low-index directions and orientations of adjacent reconstructed domains was detected with a slight preference only for steps in the [011] direction together with domains of almost parallel corrugation (4.6° off). Finally, in an extension of our comment referring to Fig. 1 we want to emphasize that we have never observed two or more domains of different orientations on a single terrace which would be evident from their different corrugation lengths.

From these results we can conclude the following: (a) The coexistence of different rotational domains on one terrace is energetically unfavorable and therefore avoided. (b) The interaction between neighboring domains on different terraces (i.e., separated by a step) is small enough to permit all combinations of domain orientations on both sides of the step. (c) The orientation of the reconstructed domain on neither the upper nor the lower terrace is dictated by the step direction. (d) The activation energy for reordering, i.e., an effective rotation of the hexagonal-reconstructed domains, is low enough to be overcome at 1100 K. (This point implies that in the initial process of nucleation, different domains of the reconstructed phase can form simultaneously on one terrace which later coalesce to a single one.)

According to thermodynamics a system will tend to minimize its free energy. From energetic reasons this postulates the existence of a single domain over the entire surface because of the higher energy of domain walls. The temperature-dependent entropy term (configurational entropy) in contrast favors a multitude of small domains. As evident from our data the reconstructed Pt(100) surface realizes the first possibility in a limited range, namely on single terraces. The interaction $E_{d\text{-}d}$ between domains of different orientation on a single terrace which determines the energy gain by removal of the domain walls must be sufficient to make this configuration (one domain per terrace) the thermodynamically most stable one even at 1100 K. Lower temperatures will favor this configuration even more. From the rather large size of the terraces we can also draw the same conclusion with respect to the removal of steps. The remaining steps are attributed to geometric constraints.

On separated terraces adjacent domains with different orientations can coexist following the pattern of initial nucleation. This also demonstrates that the surface by itself does not preferentially reconstruct in one orientation but statistically selects all possible domains in agreement with the equal intensities of the respective LEED extra patterns. The "through step" interaction $E'_{d\text{-}d'}$ between adjacent domains of different rotational orientations on both sides of a step is obviously smaller. In this case the configurational entropy term dominates and little correlation between these domains at 1100 K is observed. More surprising, however, is the small correlation between step direction and that of the corrugation ($E_{d\text{-}s}$). A step represents a severe disturbance and breaking of symmetry of the surface and, in contrast to our results, would therefore be expected to favor strongly certain orientations of the adjacent reconstructed domains. For the $c(2\times2)$ reconstruction of a W(100) surface with steps in [110] direction strong preference for one of the two possible rotational domains was found for the clean surface, while for the hydrogen-induced $c(2\times2)$ reconstruction (with different symmetry) both domain orientations were equally probable.[10] In consequence a preferential selection of rotational domains due to step-domain interaction is possible but depends on the specific character and symmetry of the reconstruction. Since on Pt(100) none of the low-index step directions is exactly parallel to a possible corrugation direction their mutual orientations are apparently almost equally unfavorable. The small effect of the step upon the reconstruction is also evident from the observation that the corrugation extends directly to the step on both adjoining terraces. For W(100) it was reported that the $c(2\times2)$ reconstruction is inhibited on stripes of ~20-Å width along steps.[11] On the basis of high-resolution LEED and EELS measurements, however, a long-range inhibition was excluded later.[12] Comparisons between the reconstructions on W(100) and on Pt(100) are also generally problematic because of the different mechanism ("displacive" versus "reconstructive") and the much higher energy difference between the reconstructed and the nonreconstructed phases in the case of Pt(100).[9]

For the Pt(100) surface the domain-domain and domain-step interaction energies respectively follow the order

$$E_{d\text{-}d'} > E_{d\text{-}s} \geq E'_{d\text{-}d'}.$$

Returning to the principle of free-energy minimization stated above, most of the energy in this case is already gained by a reduction in the number of domains per terrace, i.e., by a minimizing of the contributions from $E_{d\text{-}d}$ via coalescence and reorientation of the domains. This picture is not altered by entropy effects. Even for rather small domains of the reconstructed phase and at 1100 K, the gain from configurational entropy is small.

The rather high annealing temperatures of 1100 K used here are not required from thermodynamic reasons but from kinetic limitations. The reordering of rotational domains locked in with the substrate and with each other and the dissolution of steps require much higher temperatures than the diffusion either of single platinum atoms or of small clusters of platinum atoms on a smooth substrate.[13] The onset of reconstruction at 420 K[4] indicates some mobility of Pt atoms on the 1×1 substrate even at this temperature, since it is accompanied by at least short-range transport of Pt atoms due to density differences in the respective structures.[8]

The rather high barrier for the reordering of domains becomes evident also from the transition from the hexagonal into the rotated hexagonal structure around 1100 K.[4] In a recent structure model based on a kinematic evaluation of the LEED pattern, Moritz[17] proposed that both of these structures consist of identical 5×12 units which in the rotated hexagonal structure are regularly shifted with respect to each other, while in the hexagonal structure these shifts occur statistically in opposite directions. In this picture the hexagonal → rotated hexagonal transition as well as the dissolution of adjacent rotational domains involves a reordering of the 5×12 units; their kinetic parameters should be closely correlated. Also from energetic considerations these two processes are comparable since in both cases domain walls between 5×12 units are dissolved. Since the energy contained in the domain walls is sufficient to drive the transition from the hexagonal into the more stable rotated hexagonal phase at 1100 K, it should also be high enough to inhibit the coexistence of such different rotational domains on a single terrace.

In summary, we have shown that upon being annealed to 1100 K the clean Pt(100) surface contains terraces of typical diameters of several hundred to several thousand angstroms, which exhibit only one reconstructed domain each. Different rotational domains on one terrace are unfavorable because of the high potential energy of the domain wall. Coupling between rotational domains over monatomic or biatomic steps, in contrast, is weak and all different arrangements of domains on neighbored terraces are possible. Also the interaction between steps and the reconstructed layer is too weak to favor strongly preferential orientations.

We gratefully acknowledge the always helpful technical advice from Chr. Gerber and stimulating discussions with Dr. H. Rohrer. This work was supported by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 128.

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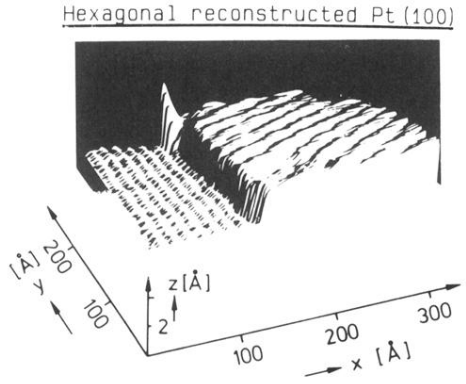

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