

Mesoscopic Self-Organization Induced by Intrinsic Surface Stress on Pt(110)

P. Hanesch and E. Bertel

Max-Planck-Institut für Plasmaphysik, Abteilung Oberflächenphysik, Euratom Association,
P.O. Box 1533, D-85740 Garching, Germany

(Received 18 February 1997)

Scanning tunneling microscopy revealed a quasi-one-dimensional periodic island structure on the clean Pt(110)-(1 × 2) surface. The period is about 1500 Å. As indicated by several test experiments, the structure corresponds to the thermodynamic equilibrium. This spontaneous island formation is attributed to mesoscopic self-organization induced by the intrinsic surface stress. It is demonstrated that such mesoscopic structures allow determination of the absolute surface stress. The present result agrees with *ab initio* calculations. [S0031-9007(97)03904-5]

PACS numbers: 68.35.Bs, 61.16.Ch, 68.35.Md

Self-organization processes, such as spatial and temporal pattern formation on surfaces, play an important role in catalytic processes [1]. Stress-induced self-organization is a common but as yet little explored phenomenon in the epitaxial growth of layered materials. It has even been proposed as a means to fabricate nanoscale structures in microelectronics [2,3]. Most of the case studies reported so far concern semiconductor systems [2–5]. Mesoscopic self-structuring on metal surfaces was observed but in most cases found to be related to adsorbates [6–8].

The present scanning tunneling microscope (STM) study of the Pt(110) surface revealed a mesoscopic, periodic surface modulation which has not been reported previously. On the atomic scale previous results were reproduced. The observed structure could be consistently interpreted as resulting from stress-induced self-organization. Absolute surface stress is a quantity not readily accessible by experimental techniques [9,10] but of great practical importance in thin film technology [10,11]. The present study opens a perspective on stress determination via monitoring the surface morphology.

The Pt crystal could be heated to about 1300 K by means of a graphite/boron-nitride oven, or cooled to about 120 K by thermal contact with a liquid nitrogen cryostat. The sample was cleaned by Ar ion bombardment ($E_{\text{kin}} = 500$ eV) and heating in oxygen ($T = 820$ K, $p_{\text{O}_2} = 5 \times 10^{-6}$ Pa) with subsequent flash to 1000 K. This yielded a clean (110) surface as judged by Auger measurements. However, temperature programmed desorption (TPD) spectra after oxygen adsorption at low temperature contained still a significant fraction of CO₂. It could be removed only by repeated cycles of oxygen adsorption at low temperature ($T < 140$ K) and subsequent desorption. For the final conditioning the TPD temperature was ramped up to 1000 K and kept there for 2 min before the crystal was allowed to cool. This procedure yielded a well-ordered (1 × 2) reconstructed surface [12]. A CO₂ TPD signal reverted after sputtering or heating to above 1100 K, although no C signal was detectable in the Auger spectra. While heating to above 1100 K occasionally yielded (1 × 3) reconstructed terraces in the initial

period of our investigations, the tendency towards (1 × 3) reconstruction gradually diminished as the accumulated number of heating cycles increased. This confirms recent conclusions of Kern and co-workers [13] associating the (1 × 3) reconstruction with residual C impurities. Br was dosed onto the crystal from a solid state electrochemical cell similar to the one described by Spencer *et al.* [14]. The STM data were acquired at 300 K in a DME [15] STM.

The morphology of the clean Pt(110)-(1 × 2) surface at various length scales is shown in Fig. 1. Figure 1(a) shows the typical morphology of {1 $\bar{1}$ 0} steps (we denote the steps by the step-staircase direction, pointing downhill perpendicular to the average step edge [16]). The “fish

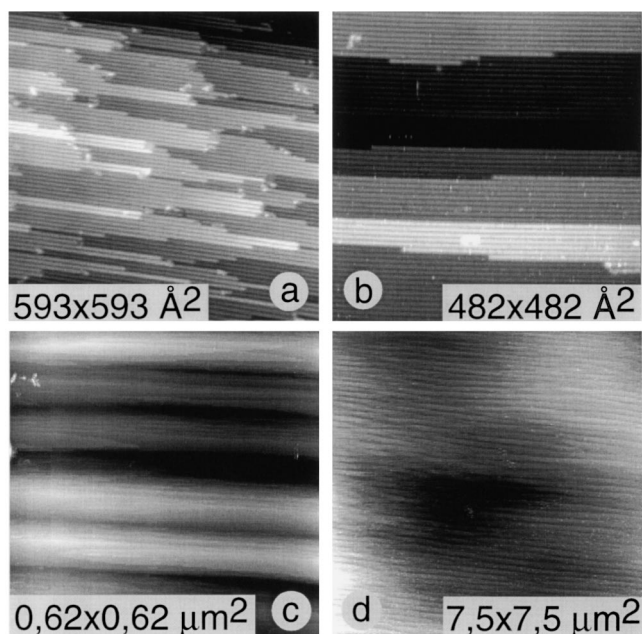


FIG. 1. STM pictures of the clean Pt(110)-(1 × 2) surface at various length scales. (a) The fish scale pattern formed by {1 $\bar{1}$ 0} steps. (b) {001} steps with their characteristically low kink density. (c) Quasi-one-dimensional, periodically arranged islands. (d) The periodic surface relief formed by the islands on a mesoscopic scale.

scale" structure shown in Fig. 1(a) has been described in detail previously [17,18]. Figure 1(b) shows an area with $\{001\}$ steps. These steps require not much energy to be formed and often extend over thousands of angstroms with only a few defects. Figure 1(c) shows the morphology on a larger scale: Ridges with a length of more than 10 000 Å in the $[1\bar{1}0]$ direction and a top-terrace width of 200–1000 Å give rise to a more or less periodic surface relief. Figure 1(d) reveals the extremely regular pattern formed by these ridges. They extend across the entire surface with a remarkably stable average periodicity of 1480 Å, which varies neither between different areas nor between different clean surface preparations. Each of the ridges is a few micrometers long. A typical cross section through three ridges as shown in Fig. 2(a) reveals an overall deviation of about 0.6° from the ideal (110) surface orientation. Superimposed on this slope are islands with a typical height of 2–4 monolayers (ML). The islands are formed by up- and downsteps created in excess of the steps originating from the misorientation.

In order to explore the origin of the island structure we carried out several test experiments. First, rotation of the sample by 90° left the structure unaffected. This excludes an external stress imposed by the sample clamping as the source of the island formation. In a second test we investigated whether the peculiar morphology is a true equilibrium structure or if it is kinetically determined. The hallmark of an equilibrium structure is its independence from the sample history, whereas a kinetically determined structure depends on previous preparation conditions. Thus in order to arrive at a clean surface from a totally different starting point as compared to our standard procedure, we used a Br dosed surface. First, a thick layer of Br was deposited onto the surface. Upon heating the surface to 780 K some Br desorbs, which results in a coverage of precisely $\Theta_{\text{Br}} = 0.5$ ML [19]. The corresponding $c(2 \times 2)$ structure develops via lifting of the (1×2) reconstruction and formation of Pt-Br-Pt chains in the $[1\bar{1}0]$ direction [20]. The energy associated with steps and consequently the step morphology is completely different from that on the clean surface. Most notably, the mesoscopic islands disappear rendering the step density significantly smaller as compared to the clean surface [Fig. 2(b)]. If

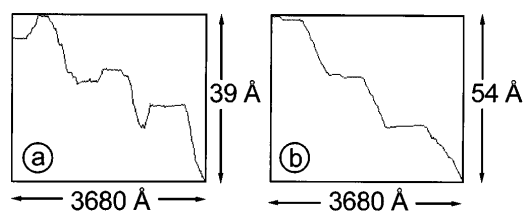


FIG. 2. Height profiles in the $[001]$ direction through (a) the clean Pt(110)- (1×2) surface and (b) through the Pt(110)- $c(2 \times 2)$ Br surface. Upon Br adsorption the islands disappear, but the periodic structuring is still visible. After flashing off the Br at 1000 K the islands reappear.

this surface is heated to 1000 K, the Br desorbs completely and the morphology of the clean surface including the islands is recovered. This proves that the additional steps are not a kinetic phenomenon due to insufficient annealing, but are spontaneously formed upon preparation of the clean surface from widely different initial states. Therefore this peculiar morphology is energetically and not kinetically determined.

Although no islands are found on the Pt(110)/Br- $c(2 \times 2)$ surface, the step density is modulated giving rise to a periodicity similar to that of the clean surface [Fig. 2(b)]. Step bunching is a possible explanation, but more likely this is a remnant of the periodicity of the clean surface before Br adsorption. At the preparation temperature of 780 K applied to obtain the Br- $c(2 \times 2)$ structure the mass transport is apparently still too slow to entirely eliminate the periodic structure. It is efficient enough, though, to flatten out the islands via local transport from the island top into the neighboring valleys. Thus the structure of the Pt(110)/Br- $c(2 \times 2)$ surface is probably kinetically dominated, in contrast to that of the clean surface, because the former still bears features of the initial state from which it was prepared, while the latter does not.

As a further test we annealed the surface to 1130 K. This yielded an island structure very similar to that obtained after annealing to 1000 K, but with an average period of 1000 Å. This period remained unaffected by further annealing experiments to temperatures $T < 1130$ K as long as no cleaning procedure was applied. If the period length was limited by kinetic effects, one would expect a larger period rather than a shorter one after annealing to higher temperatures. We attribute the shorter periodicity to an increase of the C impurity concentration. We observed a significant increase in the CO_2 desorption signal after annealing to 1130 K and subsequent oxygen adsorption at low temperature. The propensity to form (1×3) reconstructed areas was also significantly higher after annealing to 1130 K. Annealing at even higher temperatures caused a rapid increase of the (1×3) reconstructed areas. Kern and co-workers [13] demonstrated that the (1×3) reconstruction is induced by C impurities. We therefore conclude that at temperatures beyond 1100 K C segregation is sufficiently enhanced to cause an increasing C concentration at the surface and, furthermore, the increased C concentration drives the surface into a reconstruction. It is then plausible that C impurities change also the mesoscopic structure. Indeed, according to the quantitative evaluation presented below, small changes of the surface stress are expected to induce large changes of the periodicity for period lengths beyond a few hundred angstroms.

Stress-induced spontaneous formation of mesoscopic island structures on metal [7,8] and semiconductor surfaces [2–4] was reported previously. However, the only case of stress-induced mesoscopic self-organization of a

clean metal surface reported so far is to our knowledge the herringbone reconstruction of Au(111) [21]. Stress release via formation of an incoherent overlayer is obviously not viable in Pt because of the much stiffer bonding. Instead both, the small formation energy for $\{001\}$ steps on Pt(110)-(1 \times 2) and the notoriously large intrinsic stress of Pt surfaces [22], favor relaxation via spontaneous island formation. The balance between the energy gain from elastic relaxation and the energy loss from step formation determines the geometry of the island pattern [2,4]. In the following the theoretical results of Tersoff and Tromp [2] are used in order to quantitatively evaluate the surface stress from the island geometry.

The island energy per unit volume is given as $E/V = E_s + E_r$, where E_s is the formation energy of the excess steps formed on account of the surface stress divided by the island volume. Similarly, E_r is the elastic relaxation energy per unit volume due to the excess steps. The step formation energy has to be determined from separate experiments. The driving force for the elastic relaxation in the case investigated by Tersoff and Tromp [2] is the bulk stress σ_b of the uniformly strained layers within the island. For an island of height h the stress per layer adds up to the total two-dimensional island stress tensor $\sigma_{ij} = \sigma_b \times h \times \delta_{ij}$. The equivalent in the present, almost one-dimensional case is the intrinsic surface stress component σ_{yy} . In order to derive σ_{yy} from the equilibrium periodicity λ we set the derivative of the total energy $d(E_s + E_r)/d\lambda$ to zero and solve for σ_{yy} :

$$\sigma_{yy} = \left\{ \varepsilon_s n_h \left/ \frac{1-\nu}{2\pi\mu} \left[\ln \frac{\lambda}{2\pi a} - \left(1 - \frac{h \cot\beta}{\kappa\lambda} \right) \right] \right\}^{1/2}. \quad (1)$$

ε_s is the step formation energy per unit length and n_h is the island height in number of monolayers. The parameters of the island geometry h , β , and κ are defined in Fig. 3. The slightly model dependent cutoff length a is chosen as being half the nearest neighbor distance. $\nu = C_{12}/(C_{11} + C_{12}) = 0.42$ and $\mu = C_{44} = 7.6 \times 10^{10} \text{ N m}^{-2}$ are Poisson's ratio and the relevant shear modulus, respectively. The elastic constants C_{ij} of the substrate are taken from experimental values as cited by Mehl and Papaconstantopoulos [23]. The step formation energy ε_s of the $\{001\}$ steps has been determined [12,24] as $2.3 \text{ meV } \text{\AA}^{-1}$. Interestingly, ε_s can also be obtained from the step intersection angle α in areas with sufficiently low step density to exclude elastic step-step interactions [24]. From our STM data we obtain $\alpha = 16^\circ$ and consequently $\varepsilon_s = 2.45 \text{ meV } \text{\AA}^{-1}$, if we assume that the step angle equilibrates at room temperature. Using these values one obtains $\sigma_{yy}(\text{Pt}(110)\text{-(1} \times \text{2)}) 1.51 \text{ J m}^{-2}$ ($95 \text{ meV } \text{\AA}^{-2}$), which is slightly smaller than the σ_{yy} stress component of $113 \text{ meV } \text{\AA}^{-2}$ calculated by Feibelman [25] for the Pt(110)-(1 \times 1) surface.

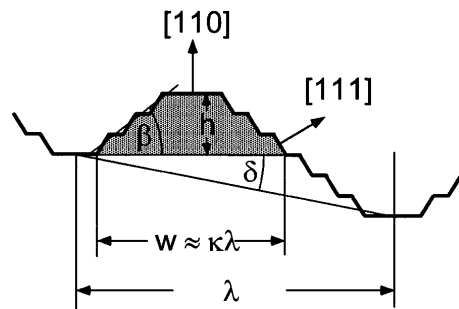


FIG. 3. Schematic cross section through an island. The sketch defines the geometric parameters used to evaluate the stress component σ_{yy} from Eq. (1). Stress-induced excess steps form regularly spaced islands (shaded). The island width $w = \kappa\lambda$ is assumed to be proportional to the period λ . From the measured misorientation $\delta = 0.6^\circ$, the average slope $\beta = 3^\circ$ of the island edges, and the average island height $h = 4.16 \text{ \AA}$ one obtains $\kappa \approx 0.80$.

We tried to obtain a measure of how much preexisting steps originating from the miscut influence the result by monitoring the periodicity as a function of the local miscut angle within a range of 0.4° up to 0.7° . Within this range the periodicity was found to be independent from the miscut. This is actually not too surprising in view of Eq. (1). The preexisting steps contribute solely to the elastic relaxation energy but not to the step formation energy. Thus taking into account the preexisting steps affects only the denominator in Eq. (1), i.e., the geometry factor $(1 - h \cot\beta/\kappa\lambda)$. As obvious from the sketch in Fig. 3, the relevant island geometry in this case is not determined by the excess island volume (shaded area in Fig. 3) but by the total island volume between two adjacent valleys. Accordingly, the geometry factor has to be adjusted. For periods as large as in the present case, however, $\ln(\lambda/2\pi a)$ is the leading term and the influence of the geometry factor is almost negligible. It is therefore not surprising that the periodicity shows no detectable dependence on the miscut angle for miscuts of the order of a few tenths of a degree. In systems with period length below about 100 \AA this dependence is expected to be more pronounced.

As an additional test for the present method of stress determination one can check whether it yields the correct stress anisotropy, i.e., $\sigma_{xx} \gg \sigma_{yy}$ [25]. With the appropriate shear modulus $\frac{1}{2}(C_{11}-C_{12})$ and assuming an island length of the order of $10\,000 \text{ \AA}$ one obtains $220 < \sigma_{xx} < 400 \text{ meV } \text{\AA}^{-2}$ for $\{1\bar{1}0\}$ step energies [18,24] $30 < \varepsilon < 100 \text{ meV } \text{\AA}^{-1}$. This is in qualitative agreement with $\sigma_{xx} = 317 \text{ meV } \text{\AA}^{-2}$ as calculated by Feibelman [25]. However, in view of the enormous island length one should be aware that the latter may not correspond to the thermodynamic limit.

Clearly, the present approach can be improved in many ways. Ideally, the stress-induced pattern should be examined on a perfectly oriented surface to exclude the

interference of preexisting steps. This is experimentally demanding, but not a principal problem. The theoretical approach involves two approximations: First, step-step interaction is not taken into account [26]. Second, the theory is based on the assumption of uniformly stressed layers within the islands. A theory including step-step interactions and an appropriate stress distribution instead of a uniform stress within the islands is desirable and certainly feasible.

In the present case both the slight miscut and the apparently rather weak step-step interaction [26] have only a small effect on the quantitative result. It agrees quite well with the *ab initio* calculation and therefore supports the assignment of the observed periodic structure to a stress-induced self-organization process. *Vice versa*, it demonstrates that stress-induced surface patterning allows one to determine the absolute surface stress from experimental data. The only other method for determination of absolute surface stress values, which was tried so far, involved evaluation of the surface phonon dispersion [27]. However, the central force model applied in this approach did not yield correct results [25,28].

In summary, the (1×2) reconstructed surface of Pt(110) exhibits a periodic island superstructure with a periodicity of almost 1500 Å in the [001] direction. The extension of the islands in the $[1\bar{1}0]$ direction exceeds 10 000 Å. The mesoscopic structure is assigned to stress-induced elastic relaxation. The stress component σ_{yy} in the [001] direction, as determined from quantitative evaluation of the mesoscopic relief, agrees reasonably well with the theoretical value obtained from *ab initio* calculations. It is concluded that stress-induced surface patterning on a mesoscopic scale may provide a method to experimentally determine absolute surface stresses.

Continuous support by V. Dose is gratefully acknowledged. We also thank K. Swamy for helpful discussions and critical reading of the manuscript. The work was supported by the Deutsche Forschungsgemeinschaft through SFB 338.

[1] R. Imbühl, Prog. Surf. Sci. **44**, 185 (1993).

- [2] J. Tersoff and R.M. Tromp, Phys. Rev. Lett. **70**, 2782 (1993).
- [3] C. Teichert *et al.*, Phys. Rev. B **53**, 16 334 (1996).
- [4] O.L. Alerhand *et al.*, Phys. Rev. Lett. **61**, 1973 (1988).
- [5] D.E. Jones *et al.*, Phys. Rev. Lett. **75**, 1570 (1995).
- [6] K. Kern *et al.*, Phys. Rev. Lett. **67**, 855 (1991).
- [7] H. Hörnis *et al.*, Phys. Rev. B **48**, 14 577 (1993). The mesoscopic structuring of Pd(110) reported by Hörnis *et al.* was apparently induced by oxygen as shown in Ref. [8].
- [8] H. Niehus and C. Achete, Surf. Sci. **369**, 9 (1996).
- [9] D.S. Campbell, in *Handbook of Thin Film Technology*, edited by L.I. Maissel and R. Glang (McGraw-Hill, New York, 1970), Chap. 12.
- [10] R.C. Cammarata, Prog. Surf. Sci. **46**, 1 (1994).
- [11] R. Koch, J. Phys. Condens. Matter **6**, 9519 (1994).
- [12] M.A. Krzyzowski *et al.*, Phys. Rev. B **50**, 18 505 (1994), and references therein.
- [13] I.K. Robinson *et al.*, Surf. Sci. **367**, 105 (1996).
- [14] N.D. Spencer *et al.*, J. Vac. Sci. Technol. A **1**, 1554 (1983).
- [15] Danish Micro Engineering, Herlev, Denmark.
- [16] E.D. Williams, Surf. Sci. **299/300**, 502 (1994).
- [17] T. Gritsch *et al.*, Surf. Sci. **257**, 297 (1991).
- [18] S. Speller *et al.*, Surf. Sci. **366**, 251 (1996).
- [19] P. Sandl, Doctoral thesis, Bayreuth, 1993.
- [20] P. Hanesch Doctoral thesis, Bayreuth, 1996.
- [21] S. Narasimhan and D. Vanderbilt, Phys. Rev. Lett. **69**, 1564 (1992).
- [22] R.J. Needs and M. Mansfield, J. Phys. Condens. Matter **1**, 7555 (1989).
- [23] M.J. Mehl and D.A. Papaconstantopoulos, Phys. Rev. B **54**, 4519 (1996).
- [24] I. Vilfan, Surf. Sci. **350**, 329 (1996).
- [25] P.J. Feibelman, Phys. Rev. B **51**, 17 867 (1995).
- [26] Our terrace width distribution is consistent with interaction free or weakly attractive steps [16]. As the elastic interaction as well as the normal component of the dipole field would rather give rise to a repulsion between identically oriented steps, the assumption of noninteracting steps seems to hold for the present case. However, the validity of the assumption has to be checked in each individual case.
- [27] S. Lehwald *et al.*, Surf. Sci. **192**, 131 (1987).
- [28] M. Balden *et al.*, Phys. Rev. B **46**, 4172 (1992).