Transition from three-dimensional to two-dimensional faceting of Ag(110) induced by Cu-phthalocyanine

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At submonolayer coverages Cu-phthalocyanine (CuPc) induces faceting of misoriented Ag(110) into three coexisting orientational phases. CuPc-decorated kinks precipitate into an azimuthally rotated facet, while the interaction of CuPc with the remaining kink-depleted steps causes step bunching in a polar transition. Local deviations from the CuPc-induced equilibrium surface morphology are caused by kinetic constraints attributed to the dominating interaction with kinks. At monolayer coverage a rigid molecular superstructure prevents large scale mass transport and allows only for microfaceting. [S0163-1829(97)02803-8]

The thermodynamic stability of vicinal surfaces, i.e., surfaces with a slight misorientation with respect to a low-index facet is governed by the free energy of the respective low-index facet, the step creation energy, and the free energy of step-step interaction. Any change of thermodynamic variables such as temperature or the chemical potential of an adsorbate which alters the relative contributions of these energetic terms may result in orientational instability of a vicinal surface. As a consequence faceting, i.e., the breakup of the surface into a ''hill and valley'' structure composed of facets with different orientation can occur.[1] The thermodynamic description of faceting emphasizes equilibrium conditions which have been achieved experimentally in only a few cases, e.g., the thermal faceting of misoriented Si(111),[2] vicinals close to Pt(100) (Ref. 3) or Pt(111) (Ref. 4) and the oxygen-induced faceting of vicinal Ag(110).[5] In all of these cases orientational instability arises from structural changes on the respective low-index facets. The formation of the (7×7) reconstruction of Si(111) and the surface reconstruction by in-plane contraction of Pt(100) and Pt(111) drives the faceting of nearby vicinals; the growth of oxygen rows on (110) terraces induces orientational phase separation on misoriented Ag(110).

Orientational instability can arise from preferential adsorption of an impurity on certain facets. However, for many adsorption systems it appears questionable whether the equilibrium theory can be applied. Three-dimensional (3D) faceting to a ''hill and valley'' surface structure requires significant mass transport and, therefore, is often kinetically hindered. At present, there is only limited knowledge about the mechanism, how kinetic phenomena determine changes in surface morphology on an atomic scale.[1] It has been argued that adsorbate-induced structures may frequently represent metastable states rather than true equilibrium configurations.[6] Considerably less mass transport is involved, e.g., in adsorbate-induced two-dimensional (2D) step faceting (microfaceting), where certain step orientations are stabilized without major mass transfer between terraces.[7,8]

Here we report the observation of a transition between equilibrium faceting and an irreversible change of surface morphology upon chemisorption. We demonstrate how the very same interaction mechanism that stabilizes new facets can inhibit mass transport and prevent phase separation. In the submonolayer coverage regime, Cu-phthalocyanine (CuPc) induces faceting of slightly misoriented Ag(110) into three coexisting orientational phases. A scanning tunneling microscopy (STM) analysis reveals the strong interaction of the CuPc molecules with substrate steps as the driving force. The molecule-step interaction is on one hand sufficient to stabilize new facets. Yet it is weak enough to allow for the mass transport on a mesoscopic scale necessary for phase separation in large parts of the surface. Local probing by STM nevertheless uncovers the signature of nonequilibrium as a result of the dominating molecule-kink interaction, which lets the phase transition partially come to a dead end in 2D step faceting. Deposition of a full monolayer yields a drastically different surface morphology. The formation of a rigid molecular superstructure on the (110) faces prevents large scale mass transport between terraces and only relaxation of the steps to a more favorable orientation along molecular rows present on the (110) terraces occurs.

The experiments were performed in ultrahigh vacuum with a custom-built low-temperature STM.[9] Samples were prepared by thermal evaporation of CuPc onto the clean Ag(110) substrate (misorientation $<0.5°$) at room temperature (RT) and subsequent annealing at ≈ 500 K for 20 min. The coverage Θ was determined by STM at 50 K. 1 ML is defined here as one molecule per 15.8 substrate surface atoms, corresponding to a dense molecular superstructure.

Figure 1(a) displays a representative STM image of the clean Ag(110) surface at 300 K. The curved steps are irregularly spaced and appear ragged.[10] After adsorption of 0.6 ML CuPc and annealing a drastic change in the morphology of the surface occurs [Fig. 1(b)]. Extended areas are comprised of (110) terraces which are separated by bunches of regularly spaced steps along $[1\bar{1}0]$. These bunches are thus depleted of kinks and can be described as $(2n+1, 2n+1, 1)$ vicinals, with $n=3$ at $\Theta = 0.6$ ML. No molecules are resolved in these areas at RT. Deposition of a full monolayer CuPc results in a strikingly different step arrangement [Fig. 1(c)]. The step orientations and spacings match the adsorbate-induced structure on the (110) facet via preferential alignment along molecular rows parallel to $[1\bar{1}1]$ and no $(2n+1, 2n+1, 1)$ vicinals are found.

The step configuration at $\Theta < 1$ ML cannot be deduced from the molecular arrangement observed on the (110) terraces at monolayer coverage. In the following, submonolayer
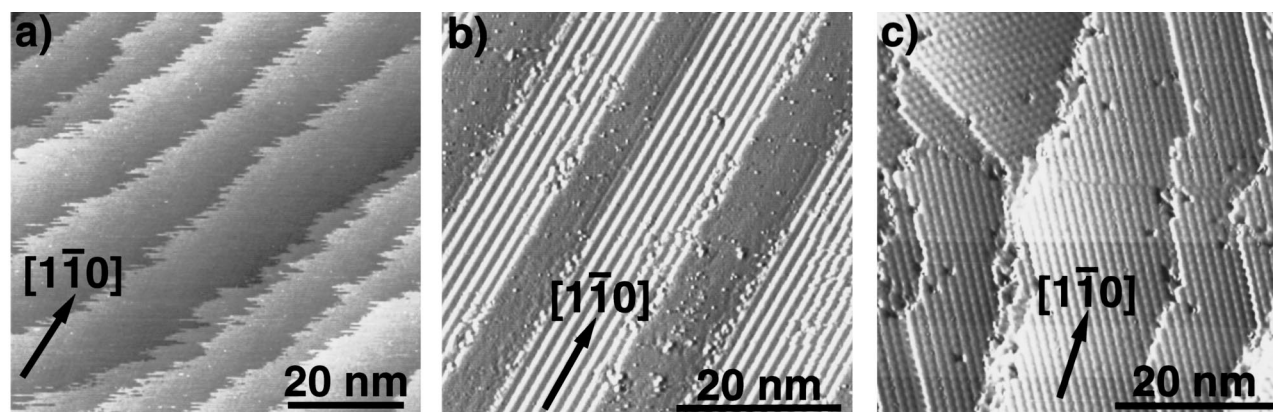
FIG. 1. (a) Clean Ag(110) surface at 300 K. (b) 3D faceted surface after deposition of 0.6 ML CuPc (300 K). (c) 2D step faceting after deposition of 1 ML CuPc (300 K).

faceting will be analyzed in more detail, focusing on two questions which arise from Fig. 1(b). First, where are the CuPc molecules and second, where are the kinks which were expelled from these areas?

At 0.3 ML CuPc [Fig. 2(a)] the steps are mainly parallel to $[1\bar{1}0]$ over large surface areas and their raggedness as well as mobility is decreased compared to the clean surface. On the (110) terraces no molecules are resolved at 300 K. However, below these steps a faint row with a width corresponding to the size of CuPc molecules (13.7 Å van der Waals radius[11]) can be discerned [inset Fig. 2(a)]. This suggests that at submonolayer coverages weakly bound CuPc is mobile on the (110) terraces at RT. An increased interaction with the steps parallel to $[1\bar{1}0]$ allows for detection with STM.[12] STM at cryogenic temperatures, where the mobility of the molecules is decreased, confirms this interpretation. For the same coverage as in Fig. 2(a) molecules are resolved on the (110) terraces at 50 K [Fig. 2(b)]. Two adsorption geometries of the individual molecules yield two different orientations of molecular chains, rotated $\pm 35°$ with respect to $[1\bar{1}0]$. These chains constitute the main structural elements of the ordered structure formed at monolayer coverage [Fig. 1(c)]. Adjacent to the (110) terraces (11, 11, 1) vicinals are found from which Fig. 2(c) reproduces a small section.

The average step spacing within the step bunches at $\Theta = 0.3$ ML (≈ 23 Å) is wider than for the vicinal areas obtained at 0.6 ML [≈ 16 Å in Fig. 1(b)]. Within bunches the density of molecules is larger than on nearby (110) facets [0.38 ML on the (11, 11, 1) vicinal compared to 0.28 ML in Fig. 2(b)], which is consistent with the proposed increased interaction with steps. Although the molecules along the step edges have the same orientation relative to the substrate as found on the (110) terraces, the narrow step spacing on the (11, 11, 1) vicinal prevents the ordering in molecular chains with the same geometry as on the open terraces; rather, a less compact arrangement along the steps is established. This indicates that a loss in intermolecular interaction energy is overcompensated by the adsorption energy at ledge sites. CuPc molecules attached to occasionally appearing kinks within the $(2n+1, 2n+1, 1)$ vicinals result in bright protrusions [arrows in Fig. 2(c)], possibly due to a bending of the molecules across the step edge.

Figure 3 provides the solution to the question on the location of the kinks. The extended kink-depleted areas are complemented by arrangements of steps with regularly spaced bright protrusions on their upper side and a chain of molecules on the lower [Fig. 3(a)]. From the 19° inclination of these steps away from $[1\bar{1}0]$ and a 12.3 Å spacing be-
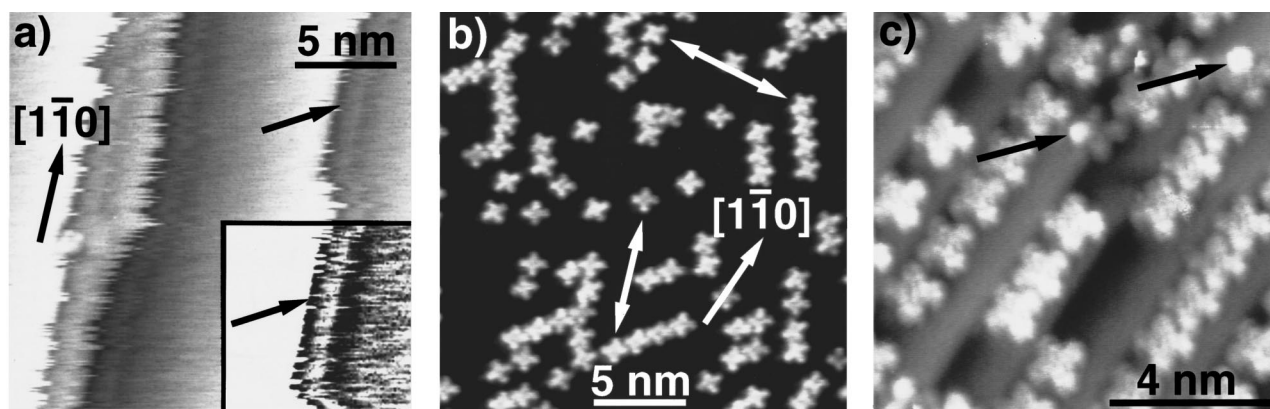

FIG. 2. (a) Step configuration at 0.3 ML CuPc coverage at 300 K. Inset: area marked by an arrow reproduced with increased contrast. In (b) and (c) different areas of the same surface are imaged at 50 K. (b) CuPc on the (110) terraces. Arrows mark individual molecules with different orientation and relate them to the respective CuPc chains. (c) CuPc on a (11, 11, 1) facet. Arrows mark molecules adsorbed at occasionally appearing kinks.
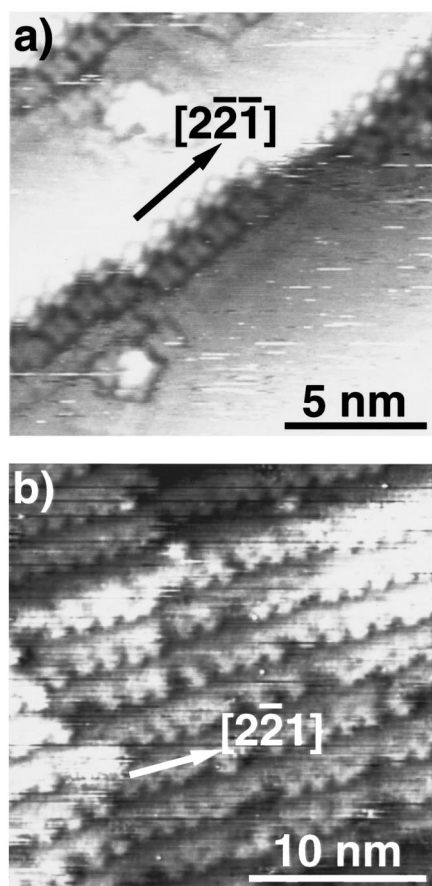
FIG. 3. (a) 1D arrangement of CuPc-decorated kinks in steps parallel to $[2\bar{2}\bar{1}]$ (0.5 ML CuPc, 300 K). (b) 2D arrangement of CuPc-decorated kinks in a (23, 24, 2) facet (0.8 ML CuPc, 300 K).

tween the bright features a model is derived where CuPc-decorated kinks are located every forth atom along the step edge, corresponding to steps parallel to $[2\bar{2}\bar{1}]$. At 300 K this structure is found to be more stable in repeated scans than steps on the clean surface. At higher coverages regular 2D arrangements of CuPc-decorated kinks in (23, 24, 2) facets exist, again with the 19° rotation of rows and the 12.3 Å distance between corrugation maxima [Fig. 3(b)]. From images not shown here we infer a CuPc configuration on the (23, 24, 2) faces identical to the one in the microfacets of Fig. 3(a).

These STM results are consistent with the following hierarchy of interaction strengths between CuPc and Ag substrate. CuPc attached to kinks constitute the most stable configuration, followed by CuPc at ledge sites and finally molecules on the bare (110) surface. Accordingly, distinct differences in the adsorption of CuPc are expected for facets with different densities of kinks and ledge sites. Preferential adsorption of CuPc changes the orientational dependence of the surface free energy[1,5] and causes an instability of the initial irregularly stepped surface. For simplicity, the observed faceting will be discussed in terms of two successive transitions, an azimuthal and a polar one. The azimuthal transition which extracts kinks from large surface areas and assembles them in the (23, 24, 2) facet is driven by the strong interaction of CuPc with kinks and the interaction among the CuPc-decorated kinks. The remaining kink-free surface areas

with steps parallel to $[1\bar{1}0]$ undergo a further, polar transition to step bunches separated by large (110) terraces. The energy scale of step bunching is set by the step-step interaction energy. On clean Ag(110) the interaction between steps is predominantly repulsive:[13] step wandering creates configurational entropy which is larger for equally spaced steps than for step bunches. The above azimuthal transition removes kinks which exist on the surface due to the azimuthal miscut. A strong interaction of CuPc with the remaining straight steps renders thermal excitation of kinks difficult. As a consequence, step propagation is diminished and the entropic repulsion between steps is decreased. The preferential adsorption of CuPc at ledge sites furthermore reduces the free energy per surface area more rapidly for facets with high step density. In combination with the decreased step repulsion this stabilizes step bunches.

The above interpretation of the CuPc-induced faceting of Ag(110) at submonolayer coverages in terms of a qualitative thermodynamic model can be further justified. The high mobility of steps on clean Ag(110) even at 300 K allows the equilibrium surface morphology of the clean substrate to be attained.[5] Therefore, the possibility that faceting results from adsorbate promoted surface diffusion[14] which allows a metastable surface to relax to its equilibrium state can be excluded. A discontinuous change of the CuPc coverage between the different coexisting phases manifests the active role of CuPc in stabilizing the newly appearing facets. Noteworthy, the (771) is the $(2n+1, 2n+1, 1)$ vicinal with the smallest step spacing stabilized by CuPc. On this facet the terrace width (14.3 Å) matches well to the van der Waals radius of CuPc (13.7 Å).

Nevertheless, there exist distinct deviations from the predictions of equilibrium thermodynamics. No clear threshold in the CuPc coverage for the onset of faceting can be discerned and phase separation is not complete. The departure from equilibrium arises from the strong interaction between CuPc molecules and kinks. The stability of CuPc-decorated steps parallel to $[2\bar{2}\bar{1}]$ [Fig. 3(a)] renders the crossing of symmetry-equivalent steps with different orientation (parallel to $[2\bar{2}\bar{1}]$ or $[2\bar{2}1]$) difficult and immobilizes them in the triangular features visible in Fig. 4(a). Kinetic hindrance thus makes the transition partly come to a dead end in 2D step faceting. This interpretation gains further support from the observation that exclusively 2D step faceting occurs when submonolayer coverages are deposited at 300 K without subsequent annealing at 500 K. Another example of incomplete phase separation is shown in Fig. 4(b), where CuPc-decorated kinks (arrows) are trapped within a (771) vicinal. These observations indicate that 3D faceting would be inhibited completely if the molecule-kink interaction strength were slightly larger. Thus the same type of interaction that on one hand stabilizes newly appearing facets can on the other hand prevent the surface to relax to its equilibrium shape. In fact, after adsorption of benzoic acid on Cu(110) solely 2D microfaceting was observed[15] which may be indicative of a molecule-kink interaction too strong to allow for 3D faceting.

In contrast to the systems discussed in the Refs. 2–5, in the submonolayer regime of Ag(110):CuPc an anisotropic change of the surface free energy arises from structural
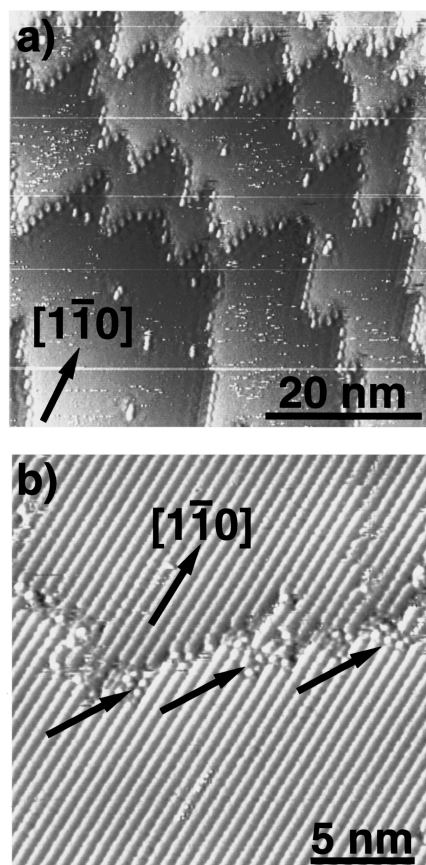
FIG. 4. Effect of kinetic restrictions at $\Theta < 1$ ML: (a) 2D step faceting. (b) CuPc-decorated kinks (arrows) trapped in a (771) vicinal.

modifications at the steps. The precipitation of kinks into a (23, 24, 2) facet is the direct consequence of the increased stability of this facet after CuPc adsorption. On the contrary, the assemblage of kinks during thermal faceting of Si(111) (Ref. 2) is a ''passive'' reaction to the formation of the (7×7) reconstruction which expels energetically unfavorable kinks from the reconstructed areas. Step bunching in

Ag(110):CuPc is due to the decreased step-step repulsion after CuPc adsorption at ledge sites and an increased adsorption energy on facets with high step density. The growth of (instable) CuPc chains on the (110) terraces [Fig. 2(b)] is supposed to play only a subordinate role in the polar transition. In Ag(110):O, on the other hand, the steps are pushed together by stable oxygen chains growing on the (110) terraces. The microscopic origin of partial irreversibility in Ag(110):CuPc may provide a general explanation scheme of why reversible faceting is observed mainly in adsorbate systems where the prevailing change of the surface free energy occurs on the low-index facet. Steps play a crucial role in surface mass transport as sinks and sources of atoms. For a dominating interaction of the adsorbate with steps the exchange of atoms may be blocked and the surface trapped in a metastable structure.

2D faceting at monolayer coverage results in a step orientation completely different from the one observed at submonolayer coverages. The CuPc-induced $(2n+1, 2n+1, 1)$ vicinals are stable for coverages close to the full monolayer [0.8–0.9 ML in Fig. 4(b)]. We conclude that even at $\Theta = 1$ the 3D faceted surface is thermodynamically stable. However, the rigid molecular superstructure prevents a major rearrangement of steps [cf. Fig. 1(a) and Fig. 1(c)] and a gain in energy can be attained only by accommodation of their orientation to the reconstruction on the (110) terraces.

In summary, we have observed on Ag(110) the transition from mainly thermodynamically controlled 3D faceting at submonolayer CuPc coverages to a kinetically dominated 2D step faceting at full monolayer coverage. Orientational instability at $\Theta < 1$ ML is caused by preferential adsorption of the molecules at steps. The observation of partially incomplete phase separation at submonolayer coverages indicates that 3D faceting would be inhibited for a slightly larger molecule-step interaction strength and manifests how kinetic constraints can result in a drastically different surface morphology.

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