# Scanning-Tunneling-Microscopy Observation of Adsorbate-Induced Two-Dimensional Step Faceting on the S/Cu(11 1 1) Surface

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Two superstructures of adsorbed sulfur coexisting on the stepped Cu(11 1 1) surface are identified by scanning tunneling microscopy. A $p(2\times2)$ and a $c(4\times2)$ structure are atomically resolved and their interaction with the steps investigated. The direction taken by a step edge is found to be strongly correlated with the sulfur arrangement on the adjacent terraces. The origin of this two-dimensional faceting phenomenon is discussed.

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The interaction between atomic or molecular adsorbates and surface defects, besides its fundamental interest, is known to play a crucial role in important technological areas such as catalysis. Vicinal metal surfaces have attracted wide attention in the investigation of this phenomenon, since they exhibit in a controllable way well defined monoatomic steps, one of the most often occurring defects on "real" surfaces. Most studies have been concerned until now with the structure and the electronic properties of adsorbed species on stable stepped surfaces, stable meaning here that no large-scale evolution of the substrate is observed. In contrast, in a few cases, a faceting phenomenon is induced by the adsorption: The surface free energy of the adsorbate-covered surface is no longer minimized and the system evolves by a change in the orientation of the steps [a phenomenon hereafter referred to as step two-dimensional (2D) faceting[1]] and/or by the formation of facets having new orientations [three-dimensional (3D) faceting[2-4]]. The understanding of these structural transitions has been largely hampered by the lack of a suitable imaging technique which could give information complementary to the results obtained by the usual diffraction techniques—mainly low-energy electron diffraction (LEED). We show in this study of the adsorption of sulfur on the stepped Cu(11 1 1) surface that scanning tunneling microscopy[5] (STM) is a very powerful technique for investigating these phenomena.

Our results include the atomic-scale observation of step 2D faceting. We find that two different superstructures of sulfur—of symmetry $p(2\times2)$ and $c(4\times2)$—develop on the Cu(11 1 1) face at 0.25 coverage. The main observation of this work is that the orientations of the steps which appear on the images are determined by the superstructure which is present on the adjacent terraces: As a consequence, only the $[01\bar{1}]$, $[01\bar{3}]$, and $[03\bar{1}]$ step directions are observed. In addition, we report on a contrast-reversal effect in a series of images, which we interpret as the consequence of a mechanical interaction between the tip and the surface.

The STM used in this study is implanted in a UHV system equipped with ion-sputtering and annealing facilities. It is similar to the "pocket-sized" microscope[6] with an additional spring stage for better vibrational isolation. Tips made by a standard electrochemical sharpening method from 0.20-mm tungsten wire were used without any further preparation. STM images were obtained in the slow scan (0.5 sec/line), constant-current mode.[5] The images presented here have been obtained with a current of 1 nA and a voltage of 1 V (sample negative). The procedure for *ex situ* sample preparation has been described elsewhere.[7] The *in situ* treatments were conducted in two steps: The sample was first cleaned by repeated cycles of argon-ion sputtering and annealing at about 870 K; then the adsorbed sulfur was obtained by segregation of the residual sulfur atoms contained in the bulk by prolonged annealing (15 min) at temperatures around 900 K. The previous Auger analyses on this sample (reported in Ref. 7) showed that this procedure systematically produces a sulfur coverage in the monolayer range.

The ideal vicinal Cu(11 1 1) surface of Fig. 1 is ob-

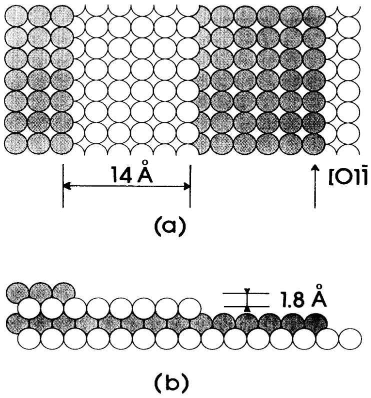

FIG. 1. (a) Top and (b) side view of a hard-sphere model of the Cu(11 1 1) surface.

tained by cutting a fcc lattice at an angle of $\sim 7.3°$ from the (100) plane in the $[01\bar{1}]$ zone. It presents $[01\bar{1}]$ monoatomic steps 1.8 Å high separated by (100) terraces of constant 14-Å width.

The STM image of a Cu(11 1 1) surface after sulfur adsorption is presented in Fig. 2(a). It shows a succession of twelve monoatomic steps, with many kinks and zigzags, but globally parallel to the $[01\bar{1}]$ direction. On the (100) terraces, a 0.3-Å corrugation reveals the coexistence of two periodic structures which are more easily visualized in Fig. 2(b), where the contrast has been locally enhanced by a statistical differencing technique.[8] The observed structures can then be described by a $p(2\times2)$ and a $c(4\times2)$ which, in agreement with LEED results on the same system,[7] we attribute to sulfur superstructures. Each bump on the image of Fig. 2(a) represents a sulfur atom. The value observed for the corrugation (0.3 Å) is in good agreement with that predicted by Lang[9] for a single sulfur atom adsorbed on a jellium imaged with a tip made of a sodium atom. We also note that a $p(2\times1)$ sulfur overlayer has been observed[10] on Mo(001) as a similar array of bumps with a 0.4-Å corrugation. The sulfur coverage, defined as the ratio of the number of S atoms to the number of surface Cu atoms is about 0.25 for the area shown in Fig. 2.

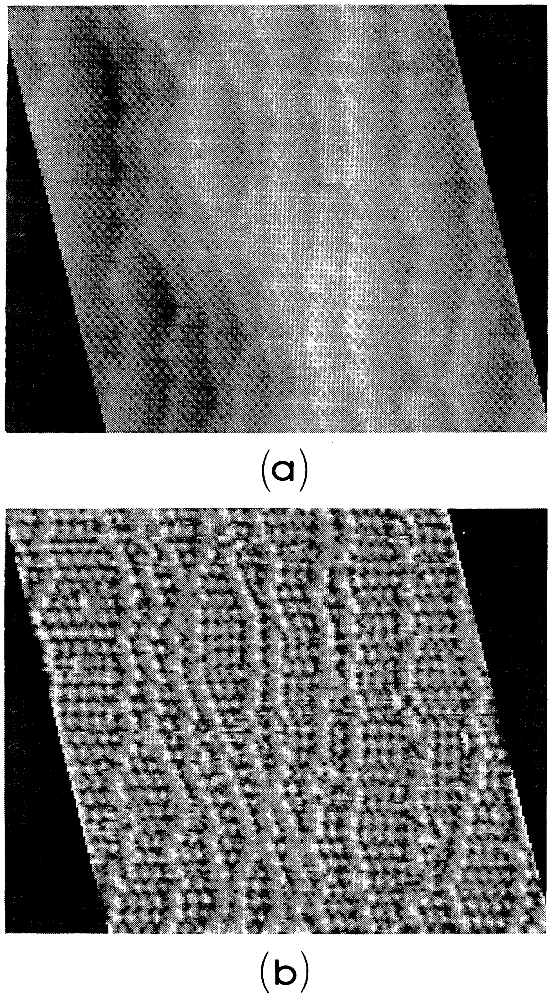

FIG. 2. (a) STM image of a $175\times145$-Å$^2$ region of a S/Cu(11 1 1) surface. The $[01\bar{1}]$ direction corresponds to the vertical. (b) Same image with contrast enhanced by a statistical differencing technique. This treatment also enhances the step edges.

The sulfur $p(2\times2)$ structure has been observed on Cu(100) by LEED.[11,12] The presence of small regions of $c(4\times2)$ ordering, coexisting with the $p(2\times2)$, has been suggested on the basis of a LEED spot-profile investigation[12] for coverages approaching 0.25. LEED[11,12] and angle-resolved-photoemission[13] studies have also demonstrated that the sulfur atoms adsorb in the fourfold hollow site of the (100) face, with a S—Cu bond distance of about 2.25 Å. On Cu(11 1 1) at 0.25 coverage, a coexistence of $p(2\times2)$ and $c(4\times2)$ is evidenced by LEED.[7] This latter study also reveals a strong selective effect of the steps; only one of the two $c(4\times2)$ domains permitted on the (100) face is observed.

Our observations, while confirming these results, show new information on the relative arrangement of both structures with steps at the atomic level. A careful examination shows that only three local step orientations appear in Fig. 2. These are, in addition to the $[01\bar{1}]$ direction of the steps of the ideal (11 1 1) face, the two equivalent directions $[01\bar{3}]$ and $[03\bar{1}]$. Moreover, these orientations are strongly correlated with the S superstructure appearing on adjacent terraces: $[01\bar{1}]$ corresponds to the $p(2\times2)$, and $[01\bar{3}]$ and $[03\bar{1}]$ to the $c(4\times2)$. This selective effect of S adsorption can be understood by simple energetic considerations: The aforementioned[12] observation of local $c(4\times2)$ ordering coexisting with $p(2\times2)$ on the (100) face indicates that both structures are close in energy. The steps which appear in Fig. 2 provide adsorption sites which are more favorable than the hollow site of the (100): step sites

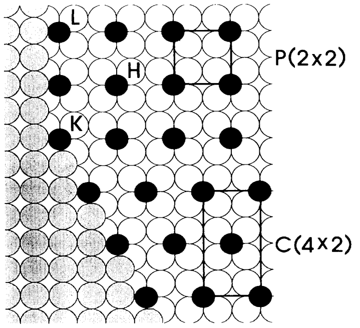

FIG. 3. Top view of a hard-sphere model of S/Cu(11 1 1). *H*, *L*, and *K* label, respectively, hollow, step, and kink sites. Open, grey, and black circles label, respectively, Cu atoms of the lower terrace, Cu atoms of the upper terrace, and S atoms.

and kink sites (see Fig. 3) where the adsorbate has respectively five and six nearest neighbors (instead of four for the hollow site). With the organization we observe in Fig. 2, the $c(4\times2)$ ordering could be favored relative to the $p(2\times2)$ because of its anchoring at the step by S adsorption on kink sites, while the $p(2\times2)$ occupies higher-energy step sites. It is then reasonable to assume that this gain in energy explains the observed step orientations. Indeed, the configuration of the kink sites of the $[01\bar{3}]$ and $[03\bar{1}]$ steps (one kink every two step atoms) fits exactly the $c(4\times2)$ structure (Fig. 3).

This 2D faceting phenomenon can be compared with its 3D analog. A strong structural relationship has been observed in many cases between the adsorption superstructure and the orientation of the facets which appear when a stepped surface evolves by 3D faceting:[7] The stable facets correspond to terrace widths which accommodate the adsorption superstructure. Our results suggest an extension of this rule to the 2D case. The step orientations observed ("2D facets") are those which accommodate the S superstructures.

The mechanism of such a transition is not established. Even the diffusing species are not known in the temperature range used to prepare our sample. One can remark, however, that the mean width of the terraces observed in Fig. 2 is near 14 Å, as on the ideal (11 1 1) face, indicating that no global transport of matter occurred perpendicularly to the steps. This is expected if the diffusion mechanism involves diffusion of kinks or sulfur along the steps.

In addition to these results, we have observed a contrast change in a series of images. The image in Fig. 4 was taken in the course of the same experiment as Fig. 2 and with identical tunneling parameters. The contrast-reversed image, Fig. 4(c), reveals features which are very similar to those observed in Fig. 2. In particular, one recognizes on the terraces the $p(2\times2)$ and $c(4\times2)$ structures. The amplitude of the observed corrugation is now about 0.9 Å instead of 0.3 Å, while the step height is unchanged at 1.8 Å. The transition between the two types of images occurs suddenly, while imaging. Therefore, we think that the contrast mechanism has changed as a consequence of a tip modification.

The contrast on constant-current tunneling images usually reflects the local density of states of the surface evaluated near its Fermi level.[14] Deviations from this simple scheme occur when the tip-surface interaction is sufficiently strong[15] and/or when a multiple tip[16,17] is involved. As shown by Mizes *et al.*,[17] the occurrence of a multiple tip can have misleading effects when imaging highly periodic surfaces such as graphite, but is easy to detect as a superposition of two or more images when the surface has a large unit cell or is not periodic as is the case here. We did not see any evidence of such an effect on our reversed-contrast images. One mechanism of contrast reversal has been proposed[18] based on a modulation of the local work function of the substrate by polarizable molecular adsorbates. We think the mechanism involved here is different. The increase of the observed corrugation to 0.9 Å cannot be explained by a mere improvement of the resolution since it is too far from the theoretical prediction[9] of 0.4 Å. On the other hand, this observation is reminiscent of the giant corrugations obtained on graphite[15] and some metal surfaces.[19] The mechanism we propose here is analogous to the proposition of Soler *et al.*[15] for explaining the giant corrugations on graphite.

The contours of total density of charge and Fermi-level density of states are shown schematically in Fig. 5 for sulfur adsorbed on a jellium.[20] While imaging in the constant-current mode the tip follows a contour of constant density of states at the Fermi level. This path devi-

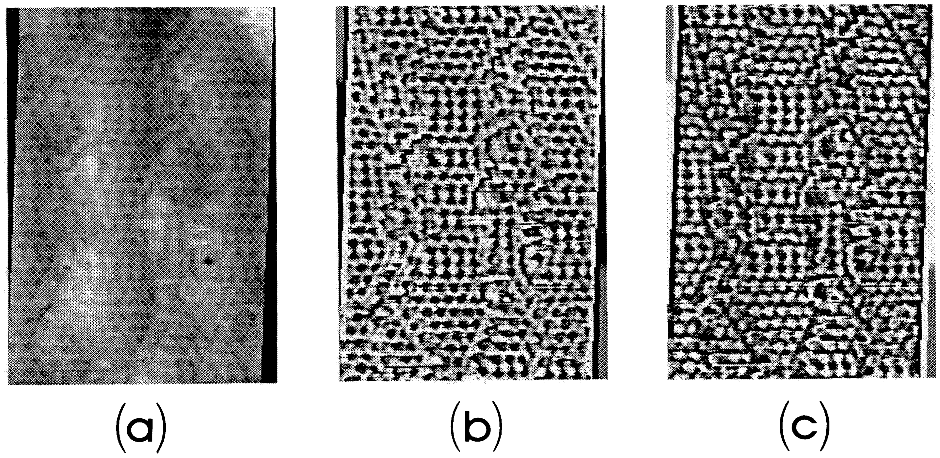

FIG. 4. (a) STM image of a 95×155-Å$^2$ region of a S/Cu(11 1 1) surface. (b) Same image with contrast enhanced by a statistical differencing technique. (c) Same image as (b) with contrast reversed.

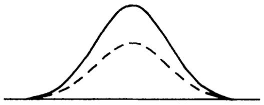

FIG. 5. Paths of total density of charge (full line) and Fermi-level density of states (dashed line) for a S/jellium surface.

ates markedly—due to the presence of the sulfur $3p$ resonance at about 3 V below the Fermi level—from the contour of constant tip-surface force, as given by the surface of constant total charge density. A spatially modulated force is then exerted between the tip and the sample. The tip-surface interaction being more repulsive just above a sulfur atom than between two atoms, one expects, if a sufficiently deformable medium is present in the tip-surface region, a "reversed giant corrugation:" The reversed contrast due to the mechanical deformation can then dominate the contribution from the local density of states at the Fermi level.

Another consequence of the strong electronegativity of sulfur is that the interaction between the tip and the surface will be stronger if a sulfur atom is adsorbed on the tip: One expects in this case a diminishing of the Fermi-level state density of the tip[9] which should be closer to the surface for a given current. Then, we suggest that the evolution from Fig. 2 to Fig. 4 is due to the adsorption of a sulfur atom on the tip.

In summary, we have presented a direct STM observation of a step 2D faceting phenomenon induced by the adsorption of sulfur on the stepped surface Cu(11 1 1). A strong correlation between the direction of the step edges and the adsorption geometry of the sulfur is demonstrated. STM on partially disordered surfaces appears extremely promising for the understanding of the mechanisms involved in such structural transitions at the atomic level.

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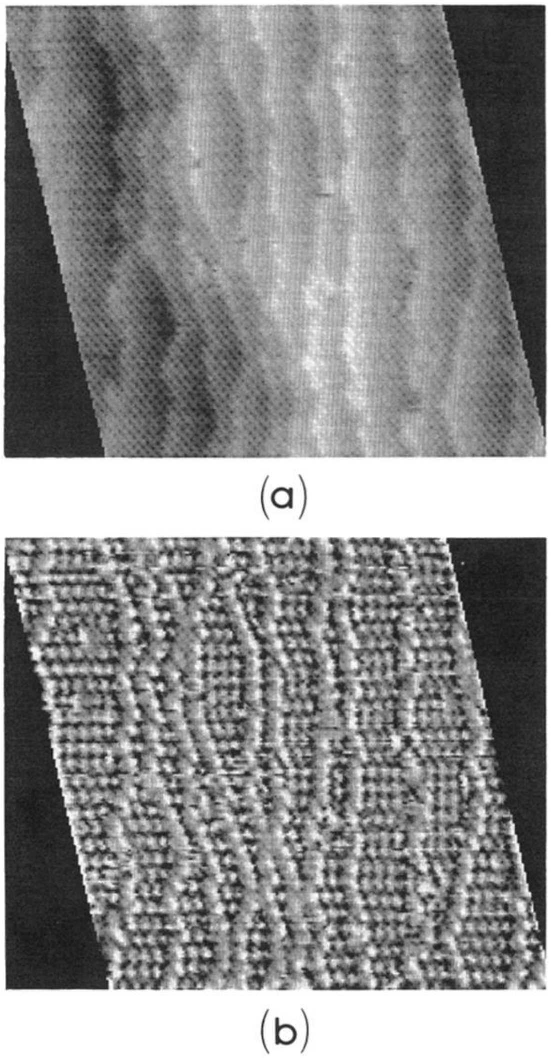

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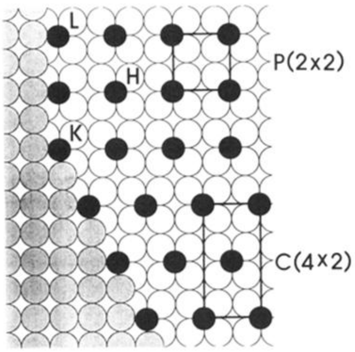

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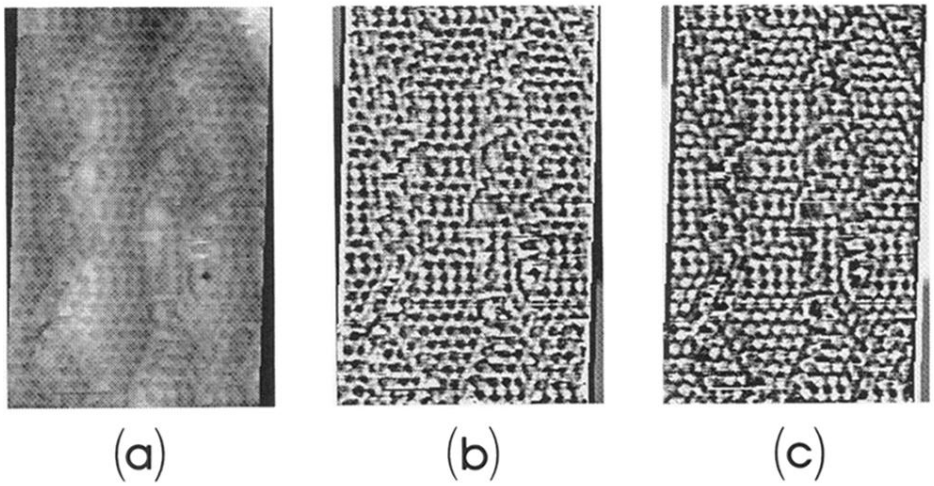

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