Frustration in the Si(111) "Pseudo 5×5" Cu Structure Directly Observed by Scanning Tunneling Microscopy

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Frustration in a surface structure has been observed in real space and time using the scanning tunneling microscope. The frustration is revealed as an instability of an inherent feature in the Si(111) "pseudo 5×5" Cu structure. A possible origin of the frustration is proposed.

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Spin glasses,[1,2] neural networks,[3] and classical optimization problems such as "the traveling salesman" problem[4] are all examples of systems with multiple, nearly degenerate "ground states": A configuration cannot be found in which competing interactions are all satisfied, and the system is said to be "frustrated."[5] For frustrated physical systems like spin glasses (as opposed to the computational problems of optimization) the possibility exists of spontaneous (physical) changes from one virtual ground state to another, and the frustration may be physically observed, rather than just exist as a computational nuisance. Indeed observed instabilities in spin glasses have been associated with frustration.[6]

Using scanning tunneling microscopy (STM) we report in this Letter what we believe are the first direct atomic-scale observations of frustration in a surface structure. Unusual dynamics of a distinct structure in the tunneling topographs of the Si(111) "pseudo 5×5" Cu structure are seen, and evidence is presented that the instabilities are due to an intrinsic frustration in the surface structure. Finally, a possible origin of the frustration is proposed in terms of a recent detailed atomic model for the pseudo 5×5 structure.[7]

The experiments were performed with a fully automated STM (Ref. 8) mounted in an ultrahigh-vacuum chamber with a base pressure of 1×10^{-8} Pa. The Si(111) crystal (Sb doped to 0.01 Ω cm) was cleaned *in situ* by ion sputtering (2 keV Ne^+) followed by annealing to 1300–1400 K. This procedure resulted in a clean and defect-free Si(111)7×7 surface as characterized by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and scanning tunneling microscopy in combination. A monolayer of Cu (7.8×10^{14} atoms/cm^2) was sputter deposited from a clean sample of 99.99% Cu using a 1-keV Ne^+ beam, and the Si crystal was subsequently annealed to 800–900 K to yield a sharp pseudo 5×5 LEED pattern.[9] All the tunneling measurements were carried out at room temperature.

Figure 1 displays examples of constant-current topographs acquired for different bias voltages. The extreme bias dependence indicates that the tunneling images are largely influenced by the surface electronic structure, and consequently geometric information cannot be readily extracted. Figure 1(a) reveals the high regularity of the surface structure in real space, and the periodicity is measured to be 20.9 ± 0.7 Å or $(5.4\pm0.2)a_{1\times1}$ in good

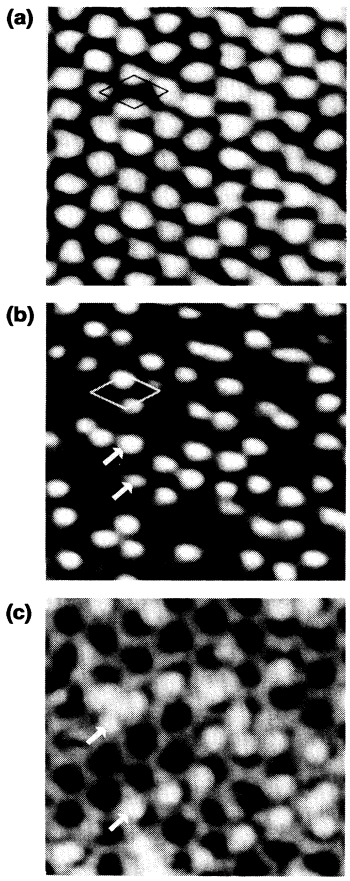

FIG. 1. Constant-current tunneling topographs of the Si(111) "pseudo 5×5" Cu surface structure. 180×180 Å^2. (a) $I_t=4.7$ nA, $V_s=0.22$ V, (b) $I_t=2.1$ nA, $V_s=0.63$ V, and (c) $I_t=1.7$ nA, $V_s=1.8$ V. (a) and (b) are of exactly the same part of the surface, and the same pseudo 5×5 unit cell is outlined. The arrows in (b) and (c) point to some of the bright featrues. The grey shading represents the tip height, with white corresponding to retraction of the tip and vice versa, and the scales are 0.5, 1.0, and 2.0 Å for (a), (b), and (c), respectively.

agreement with the periodicity found in diffraction measurements [5.60 (Ref. 7) and 5.55 ± 0.05 (Ref. 10)]. The tunneling image in Fig. 1(b) is recorded at exactly the same location, but using a higher bias voltage. Hereby, the regular structure has vanished, and new and apparently random features with diameters of ≈ 12 Å have appeared. Finally, Fig. 1(c) shows an image recorded with a bias voltage where both the regular structure (here appearing as hollows) and the bright features are visible. In this Letter we will discuss the latter feature, whereas the regular pseudo 5×5 structure will be treated thoroughly in Ref. 7.

The density of the bright features is independent of the copper coverage as well as of the annealing temperature. They always appear asymmetrically in the pseudo 5×5 unit cell, and the direction of the displacements (≈ 5 Å) away from that center of the cell is random. The asymmetry is *not* due to an asymmetric probe tip, since the directions are random within single images [see Fig. 1(c)]; rather it is a true characteristic of the surface structure. However, the bright features are randomly distributed *among* the pseudo 5×5 unit cells.

Finally, the bright features exhibit remarkable changes over time: They are observed to move within a pseudo 5×5 unit cell, to "jump" between neighboring cells, and to appear and disappear in time at room temperature, and all changes are reversible. The changes of the bright features are apparently uncorrelated, and while the rate of change is observed to span from features changing every 5–10 sec to features never changing over several minutes, a single change is instantaneous on the time scale of image acquisition (3–5 sec). This is revealed when comparing sequentially recorded images of the same location (typically 3–8 sec per 128×128-pixel image), and most vividly visualized by replaying the sequence of images at a higher speed (up to 10 images per sec) to form an STM movie.[11] Figure 2 shows six snapshots from such an STM movie, and four regions of interest in the present context are encircled.

In the following paragraph we argue that the bright features in the topographs are intrinsic and *not* additional to the pseudo 5×5 structure. As a consequence the observed instabilities are due to an inherent property of the surface structure rather than a diffusion-type mechanism.

The strong bias dependence of the bright features underscores the strong electronic character of the features, and especially the extinction at very low bias voltages provides the possibility of modeling the bright features as purely electronic features with no significant geometric (height) difference from the basic pseudo 5×5 structure.[12] Furthermore, the invariance of the density of the bright features with the amount of deposited copper strongly precludes the possibility that they are due to excess Cu or excess Si. This is also supported by the absence of any density gradient or other changes near the boundaries between pseudo 5×5 regions and clean 7×7 regions for submonolayer depositions. Finally, we note that whereas the movements within a pseudo 5×5 unit cell and between neighboring cells can be readily conceived within a diffusionlike model, the sudden appearance and disappearance is atypical for a diffusion-type mechanism and thus hard to reconcile within such a model.

Based on the experimental evidence we hence reach the conclusion that the bright features are intrinsic to the pseudo 5×5 structure, and consequently, that the observed reversible changes reflect an intrinsic instability, a frustration, in the surface structure. Having established this we will in the remaining part of this Letter take the opportunity to discuss how these new observations may possibly be explained as frustration at domain boundaries. The discussion is based on a recent model for the basic pseudo 5×5 structure,[7] and for clarity this model is briefly summarized.[13]

From a combined x-ray-diffraction, scanning tunneling microscopy, and x-ray standing-wave study,[7] it is proposed that the pseudo 5×5 periodicity is the moiré periodicity arising from placing a Cu/Si surface layer on the 1×1 template of the bulk lattice. The Cu/Si layer is presumably made by substituting half of the Si in the upper Si bilayer with a monolayer of Cu, and this Cu/Si layer is compressed vertically to a nearly planar, graphitelike structure. The vertical compression is accompanied by a lateral expansion of 9.7% and a 3.3° rotation, whereby a moiré period of $5.55a_{1\times1}$ with *no* rotation relative to the substrate lattice is constructed. Note that to obtain this periodicity all high-symmetry positions (the two threefold sites and the atop site) of either the bulk or the surface layer are assumed equivalent with regards to adlayer-substrate interactions.

An examination of this model reveals two possible ori-

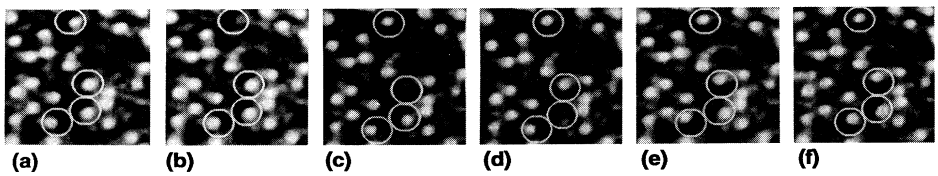

FIG. 2. Six snapshots from a sequence of tunneling images acquired at room temperature at exactly the same location. 100×100 Å^2, $I_t = 1.2$ nA, $V_s = 1.8$ V, and the grey scale is 1.5 Å. Four regions of interest are encircled.

gins for the bright features: (i) The assumption of equivalence of the high-symmetry positions may be invalid and the bright features appear at an inequivalent high-symmetry position, and (ii) the boundaries between clockwise- (CW) and counterclockwise- (CCW) rotated domains may provide odd binding configurations (possibly involving dangling bonds) giving rise to distinct electronic characteristics. The former possibility can, however, be excluded since then the bright features should order with a 3×5.55 periodicity superimposed on the 5.55 periodicity, which is not the case. Furthermore, the observation of instabilities is difficult to incorporate in such a model. The latter possibility, on the other hand, has some intriguing aspects: First, both CW and CCW domains must be present since they are equivalent, and hence domain boundaries must be present, too. Since the bright features are the only structures in the tunneling images deviating from the regular pseudo 5×5 structure, we may tentatively relate these features to the expected domain boundaries. Second, a frustration of a group of atoms at a domain boundary on whether to follow the CW or the CCW phase is readily incorporated as will be demonstrated below. It may be argued though that if the bright features are at domain boundaries, they should appear in the tunneling images as a chain and not randomly distributed as observed. Assuming, however, that the Cu/Si surface layer may relax at the boundary and thereby prevent the odd binding configurations, which give rise to the bright features, then the possibility of missing links in the chain exists, and a (nearly) random appearance in the images is plausible. With this assumption the appearance and disappearance in time of the bright features in the images is simultaneously explained.

Pursuing the idea of the preceding paragraph further we have in Fig. 3 outlined a possible situation at a domain boundary. This will illustrate how a single bright feature may move as a result of small, but collective movements of a larger group of atoms. In Fig. 3 all three high-symmetry sites of the substrate are indicated by small dots, whereas for the copper-silicon adlayer only one of the elements is depicted. To the left this layer is CCW rotated and to the right it is CW rotated. The shading of the surface layer decreases with increasing symmetry in order to better visualize the moiré pattern. At the high-symmetry positions the weak, but finite, adlayer-substrate interactions are assumed to constrain the adlayer nearly to the substrate registry. Thus regions of high symmetry are never penetrated by domain boundaries; rather they are either CCW or CW rotated. In Fig. 3(a) the center part is CCW rotated like the left-hand domain and the odd binding configurations may occur in the region just to the right of this (indicated by the question mark). Away from the high-symmetry positions the adsorbate-adsorbate interactions are dominating, and for this reason the CW-rotated region in Fig. 3(a) dominates the right-hand side, and

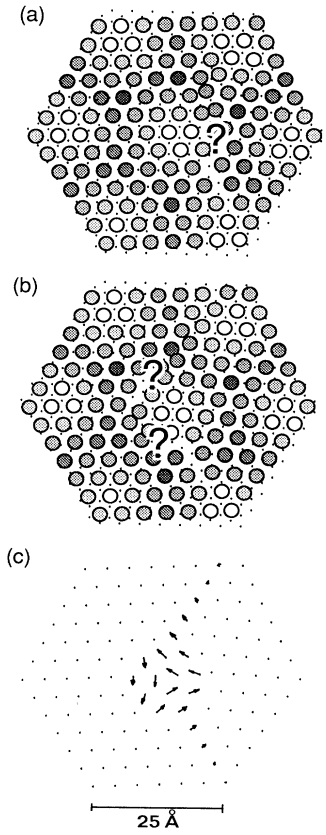

FIG. 3. Atomic model of the frustration at a boundary between $+3.3°$ and $-3.3°$ rotated domains. All three high-symmetry positions of the substrate are indicated by dots, and the circles indicate one of the elements in the 9.7%-expanded Cu/Si surface layer. The shading of the circles is coded bright when the surface layer is close to the high-symmetry positions of the substrate and vice versa. (a) The center region is rotated CCW like the left-hand part, (b) the center region is CW rotated like the right-hand part, and (c) is a map of the atomic displacements in the surface layer in going from (a) to (b).

pushes the boundary close to the center as depicted. In Fig. 3(b) the opposite situation with the central part rotated CCW is shown. A map of the atomic displacements in going from Fig. 3(a) to 3(b) is shown in 3(c), and we note how only small, but collective atomic displacements are needed to change the position of the odd binding configurations.

The above model demonstrates the possibility of modeling the observed frustration. It accounts for (i) the bright features as caused by odd binding configurations at domain boundaries, (ii) the inherent asymmetry as due to a delicate balancing of the intra-adlayer and adlayer-substrate interactions, and (iii) the observed instabilities as the frustration caused by the competition between these interactions.

In conclusion, we have observed distinct electronic features in our tunneling images of the Si(111) pseudo

5×5 Cu surface structure. These features are argued to be intrinsic to the surface structure, and the observed movements and appearance and disappearance in time of them provide direct evidence of a frustration in the structure. It is shown how this may be explained in a simple atomic model. Our observations demonstrate the feasibility of the tunneling microscope to follow dynamical processes as, e.g., instabilities in real time and space.

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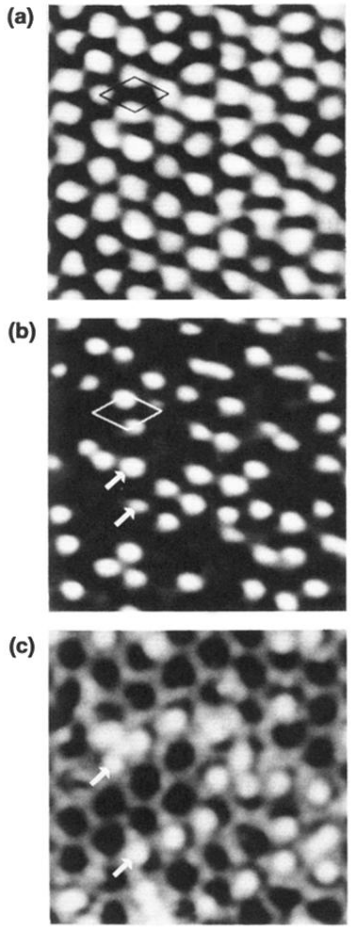

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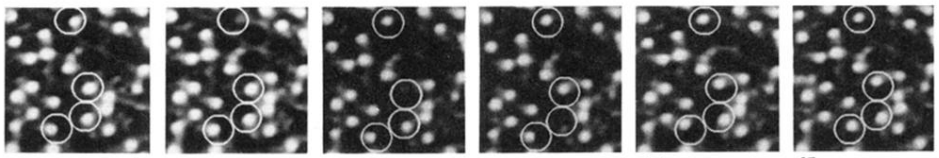

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