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Microscopic structure, discommensurations, and tiling of Si(111)/Cu-"5 × 5"

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We derive a detailed, microscopic description of the Si(111)/Cu-"5 × 5" reconstruction. The key to understanding this structure is the x-ray standing-wave determination of the Cu registry with respect to the Si substrate. With Cu basically in H_3 *and* substitutional sites the buckled Si(111) surface bilayer converts to an almost planar, hexagonal Cu_2Si layer. The straightened bond angles and the associated increase in the lateral lattice constant give rise to a hexagonal network of discommensurations of period $\approx 5.5a_{Si}$. Complete tiling of the surface requires three types of twisted (±3°) domains, two of which are rotationally equivalent.

Annealing of monolayer (ML) amounts of Cu on Si(111) leads to a most unusual reconstruction. It was described more than 20 years ago as 5 × 5.[1] Later studies revealed the noncommensurate nature of this surface reconstruction.[2,3] Since then, a puzzling variety of intriguing features has emerged. The overlayer consists of domains[3] of different types,[4,5] quasiperiodically ordered,[4,5] with about 5.55 × 5.55 periodicity.[4–6] The atomic mesh of the overlayer is 10% larger than $a_{Si}/\sqrt{3}$ and rotated by about 3°.[7] As of now there is no reconciliation of all these findings.

The present x-ray standing-wave (XSW) study provides the structural information that serves to unify the various puzzling features of the Si(111)/Cu-"5 × 5" surface structure. The key to the solution is a clear-cut determination of the registry of the Cu atoms with respect to the Si substrate. We believe that we have found a new type of discommensurate structure. The mismatched overlayer consists of an almost planar, close-packed, hexagonal layer with basically Cu_2Si stoichiometry. The structure is formed via Cu adsorbing in H_3 sites *and* substituting for Si in the upper half of the Si(111) double layer. Si remains in the lower half of the (111) double layer tying the overlayer to the substrate via Si-Si bonds. The associated energy gain competes with energy loss due to strong compressive strain in the mismatched overlayer. This leads to a hexagonal network of almost periodic discommensurations or stacking faults, giving rise to the 5.55×5.55 domain structure. Complete tiling of the surface requires, as we will show, different types of domains with the interior, noncommensurate lattice rotated by about 3°.

Cu was deposited from an effusion cell on thermally cleaned[8] Si(111)-7 × 7 surfaces held at temperatures between 570 and 650 °C. Sharp "5 × 5" LEED patterns[2] were observed subsequently. The UHV system capable of *in situ* standing-wave measurements at the AT&T, X15A beamline at the National Synchrotron Light Source (NSLS) was described previously.[9] Fluorescence from the sample was recorded while rocking the monochromator in energy through the sample reflection curve. Every preparation was investigated with standing waves using substrate (111) and (202) reflections.[10] The time lapse between the measurements was of the order of hours. Two typical XSW results are shown in Fig. 1. From a fit to the fluorescence data[11] the two parameters P and F are determined.

We investigated Cu coverages ranging from 0.3 ML (monolayers) to 3 ML where 1 ML= 7.84×10^{14} atoms cm^{-2} on Si(111). Coverage values were determined with an error of ±10% by quantitative fluorescence analysis calibrated by Rutherford backscattering spectrometry.

The determined P^{hkl} values[12] depended neither on coverage nor on preparation temperature in the investigated range. In contrast, annealing temperatures of about 650 °C were required to maximize F^{hkl}. Also, F^{hkl} values dropped for higher Cu coverages, indicating a saturation coverage of 1.3 ML in agreement with previous observations.[2]

The average P values from all investigated preparations were $\langle P^{111}\rangle = 0.98 \pm 0.01$ and $\langle P^{202}\rangle = 0.69 \pm 0.02$. The best preparations yielded maximum F values $F^{111}_{\max} = 0.8$ and $F^{202}_{\max} = 0.27$. The $\langle P^{hkl}\rangle$ values are shown in a side view of the Si(111) surface in Fig. 2(a).

Note that the intersection of $\langle P^{111}\rangle$ and $\langle P^{202}\rangle$ does not coincide with a surface site of particular symmetry. In conjunction with the finding $F^{202} \ll 1$ this proves that Cu occupies multiple sites.[11]

In Fig. 2(b) we schematically show Cu in two adsorption sites. One atom bonds to the surface in the so-called H_3 site at P^{111}=1.06, i.e., 0.19 Å above the surface diffraction plane. Another Cu atom replaces Si in the upper part of the (111) surface double layer. It is located at $P^{111} = 0.89$, i.e., 0.34 Å below the unrelaxed (111) surface diffraction plane. This corresponds to an inward relaxation of 0.74 Å compared to an unrelaxed Si surface atom position. As shown in Figs. 2(c) and 2(d), the Si(111) surface changes to an almost planar, close-packed hexagonal structure made of Cu and Si with stoichiometry Cu_2Si and lattice constant $a_0 = a_{Si}/\sqrt{3}$ (Ref. 13) where $a_{Si} = a_{101} = 3.84$ Å. $\langle P^{hkl}\rangle$ and F^{hkl} values calculated from this structure are in agreement with the standing-wave results except for F^{202}. The abnormally small observed F^{202} value is an expression of the noncommensurate nature of the surface. Since a simple incommensurate Cu_2Si surface layer would yield $F^{202} \approx 0$, the observed F^{202} value indicates that the overlayer has a domain structure where each domain has a preferred registry with respect to the substrate. In each domain Cu is distributed laterally symmetrically by about ±0.4 Å around S_u and H_3 sites. From symmetry and bonding considerations other surface sites can be excluded. With these constraints we arrive at a structure, shown in Fig. 3, which is in agreement with overlayer mismatch and rotation[7] as well as the observed domain size.[4–6]

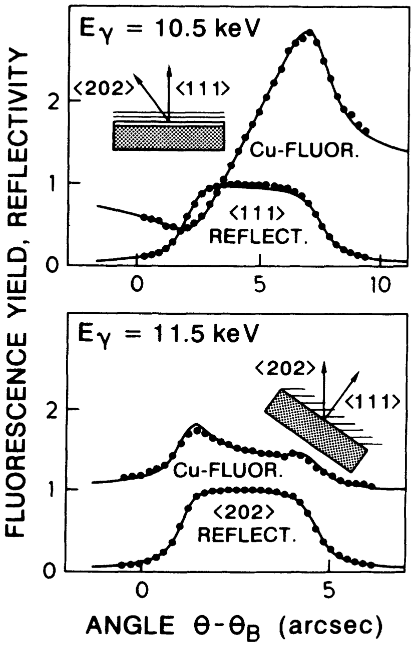

FIG. 1. Results of (111) and (202) standing-wave measurements on Si(111)/Cu-"5 × 5". 1.3-ML Cu, annealed at 650 °C. Symbols are experimental data and solid lines are fits to the data. From fitting the fluorescence data $P^{111} = 0.99$, $F^{111} = 0.81$, $P^{202} = 0.70$, and $F^{202} = 0.27$ are determined (Ref. 11). In the inset the orientation of the standing-wave field relative to the Si surface is indicated for the (111) and the (202) [tilted (Ref. 10)] measurements.

Two Cu_2Si domains are shown on the Si(111) surface in Fig. 3(a). The interior of the domains consists of a hexagonal Cu_2Si mesh as shown in Figs. 2(c) and 2(d), laterally expanded by 10%. Domains *A* and *B* are of equal size but centered at a high-symmetry surface site around a Cu and Si atom, respectively. They are connected by a lattice vector $\mathbf{a}_D = 5.5\langle 101\rangle + 0.5\langle 1\bar{2}1\rangle$, with $|\mathbf{a}_D| =$ 21.15 Å= $5.51a_{Si}$. To achieve registry at the boundary they are rotated by 3°.[14] Note that the domain boundary between *A* and *B* represents a stacking fault.[16] The Cu saturation coverage for this surface structure would be 1.6 ML, which is a little bit higher than the experimentally observed 1.3 ML. But the domain boundaries may be depleted of Cu, for instance, via predominant Si-Si bonding (e.g., dimer formation). This would explain why the boundaries show up so clearly in scanning-tunneling-microscopy (STM) measurements.[5] With 50% depletion the saturation coverage is 1.3 ML.

The calculated *P* and *F* values, with 50% depletion of

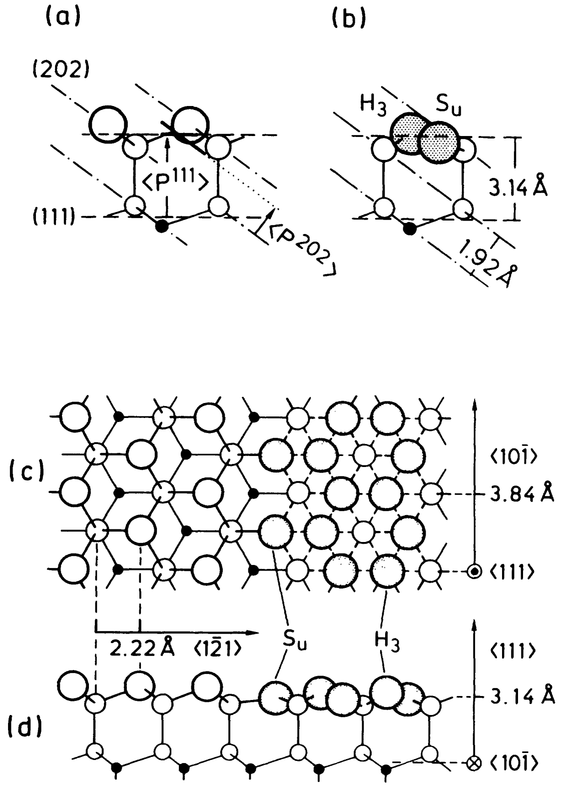

FIG. 2. (a),(b) Cross-sectional view of Si(111) with XSW results in terms of P^{hkl} (a) and resulting Cu positions (b). (111) and (202) diffraction planes, (111) surface plane, and diffraction plane spacings are indicated. (c),(d) Si(111) surface in (c) top view and (d) side view. Right-hand part of the surface is covered with Cu (shaded symbols) in S_u and H_3 sites, leading to a hexagonal structure with Cu_2Si stoichiometry.

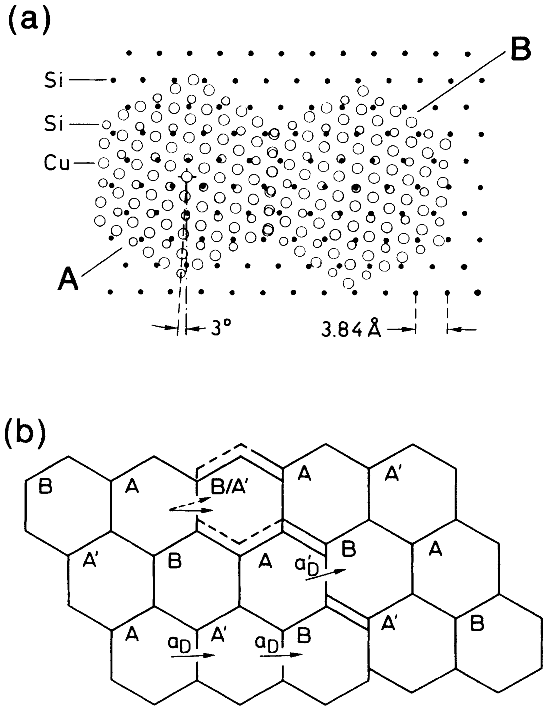

FIG. 3. (a) Two Cu_2Si domains on the Si(111) surface. The interior lattice with lattice constant $a_{Si}/\sqrt{3}$ + 10% is rotated cw by 3°. Black dots: (111) Si surface atoms; small circles: Si atoms in Cu_2Si overlayer; large circles: Cu atoms in Cu_2Si overlayer. (b) Example for tiling Si(111) with A-, A'-, and B-type domains. Correct tiling sequence is A, A', B, A, etc. Shown also are tiling defects, e.g., $A'BAB$, where A and B are connected via $\mathbf{a}'_D = 5.5\langle 101\rangle - 0.5\langle 1\bar{2}1\rangle$ creating an increase in the type-B density. Sketched is also a "frustrated domain" which fluctuates between type A' and type B.

Cu at the domain boundaries, and with the above given values for Cu positions (H_3S_u), Cu_2Si lattice constant ($a_{Si}/1.57$), and rotation angle (3°) are $\langle P^{111}\rangle = 0.98$, $F^{111} = 0.85$, $\langle P^{202}\rangle = 0.67$, and $F^{202} = 0.31$, in excellent agreement with the experimentally observed values. The bond lengths 2.49, 2.54, and 2.54 Å for Si-Cu(S_u), Si-Cu(H_3), and Cu(S_u)-Cu(H_3), respectively, are very reasonable compared to 2.35 and 2.56 Å for bulk Si-Si and Cu-Cu bond lengths.

Since Cu resides exclusively in H_3 and S_u sites, Si atoms in the Cu_2Si layer are always above Si atoms of the substrate, "anchoring" the overlayer to the substrate. The almost planar Cu_2Si layer is most likely the result of Si rehybridization ($sp^3 \longrightarrow sp^2$) similar to the situation in the Si(111)/Ga-6.3 x 6.3 surface structure.[8] In conjunction with larger Cu-Si bond lengths this generates large compressive strain in the surface layer, breaking overlayer-substrate Si bonds and creating the observed stacking faults and/or discommensurations.

A complete tiling of the surface requires equal numbers of type-B, type-A, and type-A' domains as shown in Fig. 3(b). Type-A and type-A' domains are identical except for a rotation by 180°. The correct tiling sequence is A A' B A, etc., with all domains connected via $\mathbf{a}_D$. However, we believe that the Si(111)/Cu-"5 x 5" structure is rich in tiling defects [cf. Fig. 3(b)]: (i) The Si atoms in type-B domains are on average closer to the center and thus overlayer-substrate Si-Si bonds are less stretched. Furthermore, type-B domains display a higher symmetry (inversion center). Thus, they are energetically slightly favorable. (ii) The cost in energy due to tiling defects will be moderate and thus a large amount of these defects will be in equilibrium at the growth temperature of Si(111)/Cu-"5 x 5".

Tiling defects will slightly expand the domain superlattice achieving closer agreement with the experimentally observed value of $5.55a_{Si}$. Consequently, true long-range order will be destroyed, in agreement with the results of STM (Ref. 4) and recent surface x-ray-diffraction measurements.[15]

Mortensen recently observed indications of frustration in the Si(111)/Cu-"5 x 5" structure and argued that the competition between clockwise (cw) and counterclockwise (ccw) rotated domains were the reason.[5] Takayanagi, however, investigated Si(111)/Cu-"5 x 5" and observed[7] that large areas, measuring more than 1000 Å, are rotated either cw or ccw exclusively. Here we find that within these areas rotation in one direction exclusively is *required* to obtain reasonable bonding at the domain boundaries.

The observed frustration may arise from the conflict between establishing long-range order via correct tiling and locally favoring type-B domains. Note that type-A or -A' domains easily convert to type-B domains just by moving the domains walls. The internal lattice will shift only by about 0.2 Å but the effective center of the domain, now defined by a Si atom, would change by several angstroms. This domain switching may actually happen dynamically at room temperature.

As in the present case, the basic mechanism, driving discommensurations, is competition between substrate-adsorbate and adsorbate-adsorbate interaction as already described by Frank and van der Merwe.[17] A huge body of literature has accumulated on the subject of discommensurate phases[18] and various fascinating structural aspects transpired. Villain[19] proposed the formation of semiregular adsorbate domains on a substrate with hexagonal symmetry. Furthermore he expected breathing modes, i.e., fluctuations of domain walls. Rotation of hexagonal domains was predicted, e.g., by Coppersmith *et al.*[20] Si(111)/Cu-"5 x 5" seems to resemble all of these features. Yet discommensurate phases, usually occurring during commensurate-incommensurate phase transitions, consist of almost commensurate regions of the adsorbate, separated by discommensurations (light or heavy walls[18]). In contrast, Si(111)/Cu-"5 x 5" consists of domains, the interior of which is incommensurate, separated by stacking faults (light walls).

In summary, locating Cu in the Si(111)/Cu-"5 x 5" reconstruction identifies the reason for the domain structure. Compressive strain in the planar Cu_2Si overlayer causes disruption of Si bonds to the substrate. Discommensurations and/or stacking faults arise, separating domains, tied in the center to the substrate via Si-Si bonds.

Equal numbers of type-A, -A', and -B domains, with a noncommensurate interior lattice rotated by ≈3°, are needed for a perfect tiling of the surface. B-type domains seem to be energetically slightly favorable. This leads to an increase in the B-type population ultimately destroying long-range order. The defective domain superstructure most likely gives rise to frustrations observed recently by STM.[5]

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[11] See, e.g., J. Zegenhagen, G. Materlik, and W. Uelhoff, J. X-ray Sci. Technol. **2**, 214 (1990).

[12] P^{hkl} values can be converted to distances Z^{hkl} normal to the used diffraction planes simply via $Z^{hkl} = P^{hkl}d^{hkl}$, where d^{hkl} is the diffraction plane spacing (Ref. 11).

[13] The lattice constant is only $a_{\rm Si}/\sqrt{3}$ if we do not distinguish between Si and Cu. Justification for this will be given below.

[14] A recent x-ray-diffraction study (Ref. 15) found a slight spiral rotation of the domains of about 3° and basically confirmed the overlayer lattice constant.

[15] F. Grey, R. Feidenhans'l, M. Nielsen, R.L. Johnson, and J. Zegenhagen (unpublished).

[16] The interior of each domain consists of a Cu_2Si lattice (cf. Ref. 2) with lattice constant $a_{\rm Si} \times 1.1$. But by crossing a domain boundary (stacking fault) Cu and Si positions are exchanged. Thus, the overlayer as a whole appears like a hexagonal lattice with lattice constant $(a_{\rm Si}/\sqrt{3}) \times 1.1$, where the sites are occupied by either Cu or Si.

[17] F.C. Frank and J.H. van der Merwe, Proc. R. Soc. London **189**, 205 (1949).

[18] See, e.g., P. Bak, in *Chemistry and Physics of Solid Surfaces V*, edited by R. Vanselow and R. Howe (Springer-Verlag, Heidelberg, 1984); R.F. Willis, in *Dynamical Phenomena at Surfaces, Interfaces, and Superlattices*, edited by F. Nizzoli, K.H. Rieder, and R.F. Willis (Springer-Verlag, Heidelberg, 1985), and references therein.

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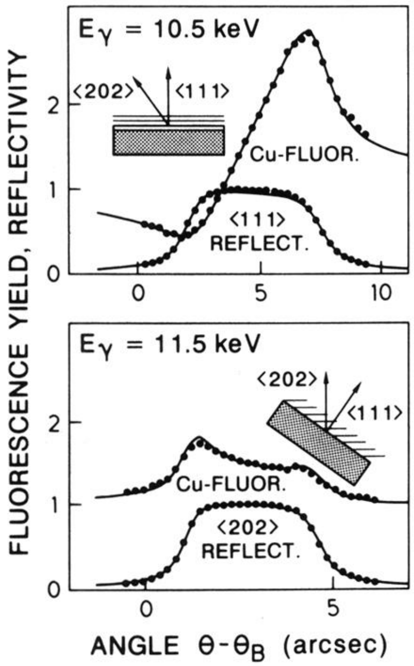

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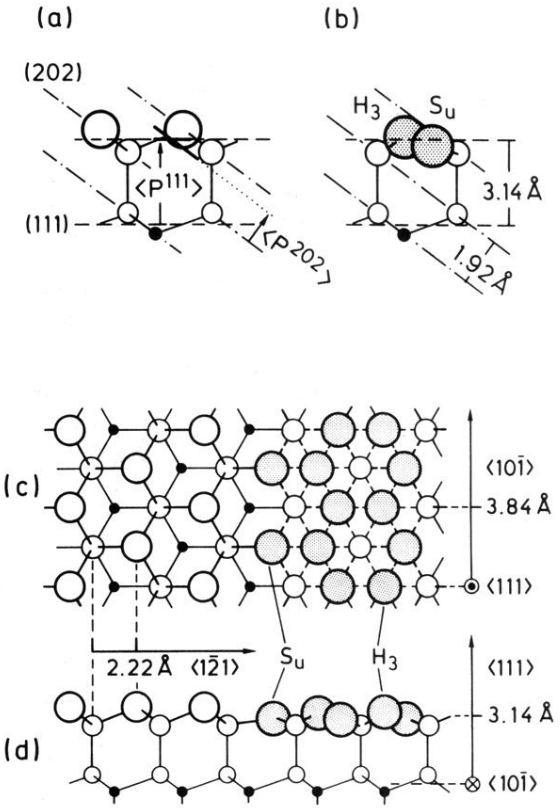

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