Atomic-Scale Imaging of the Surface Dipole Distribution of Stepped Surfaces

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ABSTRACT: Stepped well-ordered semiconductor surfaces are important as nanotemplates for the fabrication of 1D nanostructures. Therefore, a detailed understanding of the underlying stepped substrates is crucial for advances in this field. Although measurements of step edges are challenging for scanning force microscopy (SFM), here we present simultaneous atomically resolved SFM and Kelvin probe force microscopy (KPFM) images of a silicon vicinal surface. We find that the local contact potential difference is large at the bottom of the steps and at the restatoms on the terraces, whereas it drops at the upper part of the steps and at the adatoms on the terraces. For the interpretation of the data we performed density functional theory (DFT) calculations of the surface dipole distribution. The DFT images accurately reproduce the experiments even without including the tip in the calculations. This underlines that the high-resolution KPFM images are closely related to intrinsic properties of the surface and not only to tip–surface interactions.

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step edges display the surface corrugation and periodicity of the
(7 × 7) reconstructed areas, respectively.

To discuss the structure of the surface, we plotted 3D and
2D SFM images in Figure 2. We use the notation introduced by
Teyss et al.2 In the images, a (7 × 7)-reconstructed
Si(111) terrace is followed by a triple step and the next (7 × 7)
terrace. The triple step (S1, S2, S3) consists of several adatoms and
dimers rows. S1: On the edge of the upper terrace, the last
row of silicon adatoms (denoted as A1, the index indicating the
layer) is accompanied by a row of parallel dimers (D1⊥). S2: The
lower layer (index 2) is formed by a row of adatoms (A2). Often
atomic defects are observed in the A2 row at the places
where corner vacancies of the (7 × 7) surface and no D1∥ dimers
are found (these defects are denoted as RD). Such RD appear
due to the mismatch between the 2-fold periodicity of the
dimer rows and the 7-fold periodicity of the terraces. At the
RD, the adatom is shifted toward the step, as indicated in
Figure 2b. In Figure 2c, profiles over a defective and
nondefective step line of Figure 2b are shown, and the place of a RD
is indicated. Below the row of A2, we found rows of
perpendicular and parallel dimers (D1∥, D1⊥, respectively). Many
dimers are missing in the FM-SFM image, especially in D1∥. S3: Below the dimers, two extra rows of silicon atoms are
observed, the ZR row, reported from STM analysis to have a
zigzag structure,2 and the R row located at the bottom of the
triple step. The presented SFM image coincides almost one to
one with the empty-states STM image obtained by Teyss et al.2
In the case of silicon, the empty states are the fingerprint of the
free dangling bonds. This supports that the SFM image arises
from covalent bonding of the tip apex with the surface atoms. A
more detailed SFM and DFT analysis of the atomic structure of
the triple step and a rigorous comparison with the STM data
will be presented in an upcoming publication.

Figure 3 displays simultaneous topographic FM-SFM and
KPFM images measured over a terrace, the triple step, and the
next terrace. In the topographic image, Figure 3a, several
defects are observed at step edges that we previously attributed
to Si clusters. Furthermore, many atoms are missing in the D1∥
and A2 rows. In the Kelvin image, Figure 3b, strong surface
potential variations on the terraces and the step are observed.
Considering the background local CPD (LCPD) obtained at
positions between adatoms and at the bottom of the step as the
reference value (ca. 0.35 V), we discuss the values of the LCPD
as higher or lower than this reference. Thus, the adatoms of the
(7 × 7) terraces have the lowest LCPD, 0.1 to 0.2 V in our
image, in accordance with previous reports on flat Si(111).17,19
The defects at step edges (Si clusters) have a similar LCPD to the
adatoms, supporting that they are composed of additional
Si atoms. The R row and A2 adatoms also have a low LCPD
compared with the reference but slightly higher than the
adatoms and clusters. The ZR row shows almost no contrast
difference with respect to the background. On the contrary, the LCPD appears slightly higher than the
background. Also, in the region between the adatoms of the (7 × 7) terraces (restatoms), a higher LCPD is imaged (≥0.4 V).
Remarkably, the region of the dimers, in particular, at D1∥ and D1⊥, shows a high LCPD (ca. 0.5 V).

Over the (7 × 7)-reconstructed terraces, the general
contrast and the absolute value of the local contact potential
difference is in agreement with previous KPFM studies also
performed together with FM-SFM.17 Sadewasser et al.
considered several factors as a possible origin of the atomic
contrast: a possible tunneling current flow between tip and
surface, the modulation of the surface dipole, and the in
fluence produced by a tunneling
current flow between tip and surface. The tunneling probability
is different at different atomic sites (as reported from STM images\(^2\)). This may affect the strength of the LCPD, but we believe this effect to be small because the current flow is below the detection limit of our experimental setup.

We continue with the work function that is generally determined by the surface dipole, which reflects the charge distribution on the surface.\(^1\)\(^7\),\(^2\)\(^0\) To better understand the measured Kelvin contrast, we performed DFT calculations of the electrostatic surface potential. The tip is excluded for directly obtaining information on the physical properties of the surface and not on the deviations caused by the interaction of the surface with the tip. We define the local work function \(\Phi_{\text{loc}}\) at a point \(r\) near the surface as \(\Phi_{\text{loc}}(r) = V_{\text{eff}}(r) - E_F\), where \(V_{\text{eff}}(r)\) is the single-particle effective electrostatic potential and \(E_F\) is the Fermi energy.\(^2\)\(^1\) The calculated \(\Phi_{\text{loc}}\) is shown in Figure 3c. The overall behavior of the local work function along the surface is remarkably well reproduced by the simulations. For the discussion of the data, we divide the surface into two parts: the well-known (7 \(\times\) 7) reconstructed terraces and the triple step.

The local atomic dipole distribution on the flat Si(111)-(7 \(\times\) 7) surface was investigated by Cho and Hirose.\(^2\)\(^2\) They detected dipole moments pointing upward on the Si adatoms, whereas the dipole moments pointed inward at the interstitial sites between Si adatoms.\(^2\)\(^2\) This behavior was also observed in ref \(^1\)\(^7\) and is consistent with the results of this work. We can relate these dipoles to the different charge distribution on the different atoms, that is, at the lower-lying restatoms the partial negative charge is larger than at the more protruding adatoms.

At the triple step we find a striking agreement between our experimental results and our simulations. The upper part of every step of the triple step displays a lower electron density (i.e., lower LCPD), while the bottom of the steps shows a higher one. The DFT calculations (Figure 3c) reveal that the high electron density is associated not only with the dimers but also with the Si restatoms that lie in the lowest part of every step. At the upper part of the triple step, close to the D\(_{1\parallel}\) dimer row, the electron density is lower. At the bottom of this step (S\(_1\)), located between two RDs and between the D\(_{1\parallel}\) dimers and A\(_2\) adatoms, there are two restatoms denoted as RA\(_2\). These appear as bright features in the experiment and simulations. The A\(_2\) adatoms at the upper part of the second step (S\(_2\)) show a lower \(\Phi_{\text{loc}}\) while between D\(_1\) and D\(_{1\parallel}\) at the bottom they display a high one. Again at the upper part of the lower step (S\(_1\)), between D\(_{1\parallel}\) and ZR, the electron density is lower. Finally, at the bottom of S\(_1\), between ZR and R, the electron density is high. There, we find additional restatoms, denoted as RB, which are the deepest located atoms within the reconstruction with dangling bonds. Further details of the discussion of the DFT data have been included in the Supporting Information.

One important difference between our simulations and experimental results is that at the bottom of the triple step, at RB, the partial negative charge appears much larger in the calculations than in the Kelvin image. For Figure 3c, the potential was calculated at a simplified constant mean tip–surface distance value of 0.325 nm that follows the black solid line indicated in Figure 2a. Because of the presence of steps, the mean distance between tip and sample varies strongly in the experiment during the scan compared with the measurements.

Figure 3. Atomically resolved (a) FM-SFM and (b) simultaneously obtained Kelvin image at RT. (c) Calculated local work function from the electrostatic effective single-particle potential. The local contact potential difference is large at the bottom of the steps and at the restatoms on the terraces, whereas it drops at the upper part of the steps and at the adatoms on the terraces.

Figure 4. (a) Schematic side view of the Si(7\(\times\)10)-(16\(\times\)14) model of the structure. The purple curve represents the experimental line profile (Figure 2c), adjusted to scale. The black solid and turquoise dashed lines indicate the height profiles at which the local work functions \(\Phi_{\text{loc}}\) in (b) and (c) have been calculated, respectively. The turquoise dashed line is closer to the measured line profile.
over a flat surface. Hence, to reproduce the experimental conditions, we calculated again the potential, this time allowing the tip to follow a profile closer to the true height of the tip in the experiment. In Figure 4a, the corrected profile is shown as a turquoise dashed line. This line matches better the experimental profile obtained during scanning, which is marked in purple in Figure 4a (from Figure 2c). Performing this correction to the height profile in the simulation of the surface dipole results in a more diffuse and less bright feature at the bottom of the triple step, in closer agreement with the measured Kelvin image; see Figure 4b,c.

Finally, we analyze the influence of the formation of chemical bonds between the tip apex and surface atoms. In ref 17 bond formation was reported to induce a local redistribution of the charge density, leading to a change of the surface dipole and, consequently, to variations of the local chemical potential. A strong redistribution was identified for close tip–surface separations, whereas this was reduced for larger ones. In Figure 4a, we observe that at the stepped region the height of the tip in our experiment is higher than at the flat part, pointing to a weaker effect of this bonding formation in the KPFM images in this region. This argument reinforces the close agreement of experiment and simulations even without taking into account the effect of the tip in the calculations. This agreement is not only qualitative but also quantitative. The differences between the work function at the adatoms and restatoms are around 0.5 to 0.6 V in the calculations, very close to the 0.4 V in the experiments.

The electronic structure of the surface is the result of the balance between two contributions: the reconstruction-induced electron transfer due to orbital splitting and the charge separation at the upper and lower parts of the steps by analogy to the Smoluchowski effect. The Smoluchowski effect is known for metallic surfaces. 23 Smoluchowski stated that the electronic density at step edges follows the step edge more smoothly than expected from prolonging the bulk electronic density, creating a dipole pointing upward. We find the latter contribution to be the dominating one. Thus, we can interpret the KPFM image as a direct picture of the different charges of the step dipoles, which gives rise to an alternating variation of charge and therefore an alternating Kelvin contrast. An schematic representation of this charge distribution is shown in Figure 5.

Figure 5. Simplified scheme of the charge distribution at the triple step and the following (7 × 7) reconstructed terrace.

In summary, we demonstrate that FM-SFM and KPFM are able to provide simultaneous atomic resolution of the topography and the surface potential distribution, even at stepped surfaces. For a better understanding of the KPFM image, we performed DFT calculations of the electrostatic surface potential, obtaining a striking agreement with the experiments, even without including the influence of the tip. We observe a large LCPCD at the restatoms, whereas it drops at the adatoms. We explain the origin of these features in terms of the local environment of the atoms and partial charge transfers. This explanation is general and not unique to Si surfaces, which serve as model system. The DFT calculations uncover the nonnegligible contribution of the different restatoms on the surface to the surface dipole and the influence of the tip–surface distance. These results demonstrate that the observed KPFM atomic contrast is not only produced by the interaction with the tip but indeed also reflects an intrinsic property of the surface.

■ ASSOCIATED CONTENT

# Supporting Information
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Experimental methods. Numerical methods. Details of the DFT calculations of the surface dipole. (PDF)

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■ REFERENCES


