Magnification effects in scanning tunneling microscopy: the role of surface radicals

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Abstract

Scanning tunneling microscopy (STM) is a fundamental tool for determination of the surface atomic structure. However, the interpretation of high resolution microscopy images is not straightforward. In this paper we provide a physical insight on how STM images can suggest atomic locations which are distinctively different from the real ones. This effect should be taken into account when interpreting high-resolution STM images obtained on surfaces with directional bonds. It is shown that spurious images are formed in the presence of polarized surface radicals showing a pronounced angle with respect to the surface normal. This issue has been overlooked within the surface science community and often disregarded by experimentalists working with STM. Without loss of generality, we illustrate this effect by the magnification observed for pentamer-like structures on (110), (113) and (331) surfaces of silicon and germanium.
The study of the atomic structure of a crystal surface often starts with scanning tunneling microscopy (STM) measurements. The positions of bright spots in high resolution STM images are then associated with exact atomic coordinates on the surface under scrutiny. Although being generally accepted, such a connection is known to be imperfect with several deceiving cases being known. The STM images obtained from Bi-terminated Si(111) and Ge(111) surfaces are clear examples\(^1,2\) — while bright spots are observed atop of the Bi trimers at negative bias and at large positive bias, at low positive bias the spots are observed between trimers, where no atoms exist.

It is clear that the interpretation of high-resolution STM images is not straightforward. According to a simplified view, STM images obtained in a constant-current mode represent a combination of surface topography and local density of electronic states.\(^3,4\) Consequently, a full reasoning of such images, may only be possible upon some knowledge of the surface atomic structure (which is often unavailable), or with the assistance by \textit{ab-initio} electronic structure calculations.

While the connection between the surface atomic positions and bright spots in STM images is often factual and correct (and so it may be the resulting model), we show below that surface geometry misassignments are likely to occur when the electronic polarization and hybridization of states at surface atoms are overlooked. We illustrate the occurrence of large offsets between bright spots from STM images and the corresponding atomic nuclei with help of a paradigmatic example, namely with the magnification of pentamers as seen
in STM images of Si(331).\textsuperscript{5} Analogous pentameric structures were found on (110) and (113) surfaces of silicon and the (110) surface of germanium.\textsuperscript{6-8}

Figure 1(a) depicts an experimental high-resolution STM image at positive bias ($U = +0.8 \text{ V}$) of the Si(331)-$12 \times 1$ surface showing bright pentameric features.\textsuperscript{5} The bright spots at the corners of one of the pentamers are connected by dashed lines. The distance between two nearest spots is about 3.5 Å as derived from the experimental STM image in Fig. 1(a).

Figure 1(b) shows the 8P atomic model for the Si(331)-$12 \times 1$ reconstruction,\textsuperscript{5} along with its respective STM image obtained from the calculated LDOS at positive bias (considering states up to 0.8 eV above the Fermi level) within the Tersoff-Hamann approximation.\textsuperscript{3} The image in Fig. 1(b) represents the height at constant integrated LDOS between $+0.8 \text{ V}$ and Fermi level for Si(331). It gives an idea of how an STM image of the Si(331) surface would look like for an infinitesimally sharp tip, \textit{i.e.} close to a single atom with an $s$-orbital. The distance between the nearest bright spots within the pentamers of Fig. 1(b) agrees well the analogous distance as derived from the experimental STM image of Fig. 1(a). However, the overlaid atomic structure shown in Fig. 1(b) clearly shows that the actual distance between nearest Si atoms in each pentamer is 2.3 Å, corresponding to an experimental deviation of more than 50% with respect to atomic positions. Due to its magnitude, this mismatch sustained an argument against atomic models of (110) and (331) silicon surfaces involving five-fold rings of Si atoms.\textsuperscript{9-11}

Figure 2 shows a \textit{vertical} cut of the height at constant integrated LDOS (between $+0.8 \text{ V}$ and Fermi level) across the ‘A’ dashed line of Fig. 1(b) ([\overline{1}1\overline{6}] crystallographic direction) combined with a projection of a pentamer atomic structure. The brightest spot at the upper right corner of Fig. 2 shows a high intensity for the empty LDOS located near the Si radical at the upmost apex of the pentamer in Fig. 1(b). Clearly, the radical state does not point upwards (along [331]), rather making an angle of about 22° with respect to surface normal and away from the center of the pentamer. Since STM is intrinsically sensitive to LDOS,\textsuperscript{3} and because the tip usually hovers between 4 to 10 Å above the surface,\textsuperscript{4} it becomes evident
Figure 1: (a) Experimental high resolution STM image of the Si(331)-12 × 1 surface. \( U = +0.8 \text{ V}, I = 0.024 \text{ nA} \). (b) Calculated STM image of the Si(331)-12 × 1 surface within the 8P-model of Ref. 5 (atomic positions are overlaid) using a voltage that corresponds to states up to +0.8 eV above the theoretical Fermi level. Dashed pentagons in (a) and (b) illustrate the apparent size of pentamer features as derived from the center of bright spots. Dashed lines marked by ‘A’ and ‘B’ are supporting directions used in the text for discussion. Vertical and horizontal edges of the images are along [\( \overline{1}16 \)] and [\( \overline{1}10 \)] crystallographic directions, respectively.
Figure 2: Vertical cut of the LDOS along the ‘A’ dashed line of Fig. 1(b), integrated over a 0.8 eV energy window above the calculated Fermi level. The intensity (brightness) is represented on a logarithmic scale. The projection of a pentamer atomic structure is overlaid. Solid black lines show horizontal and vertical directions with respect to the surface. The dashed line is drawn from the apex atom along the direction of maximum intensity of nearest bright spot. Vertical and horizontal edges of the image are along [331] and [1̅1̅6] crystallographic directions, respectively.

that the slanted radicals will project a magnified image of the underlying pentamer. This explains the apparent contradiction between the size of the pentamers from the atomistic model and those derived directly from STM images (see Refs. 9 and 10).

The distortion of the pentamers as observed by STM should not be confused with another spurious effect which arises from the finite size of the STM tip. The measured surface topography can be represented as a convolution of the real surface topography and the shape of STM tip.12 This effect leads to broadening of the objects protruded out of the surface for the case of a dull tip. Comparing experimental and calculated STM images in Fig. 1, we realize that the image in Fig. 1(a) is indeed affected by the latter effect – the experimental image is more diffuse than the calculated one. The contribution of the finite tip size effect to the magnification of the pentamers must be however minor. A 50% increase of the pentamer size (as observed in Fig. 1(b)) would imply a severe and inhomogeneous broadening of the bright spots, which would not fit the experimental data.

Figure 3 shows the height profiles measured across the bright spots in the calculated STM
Figure 3: Height profiles along dashed lines ‘A’ and ‘B’ in Fig. 1(b) with origin at the center of a pentamer. The position of the atomic nuclei at the pentamer vertices is indicated by a dashed line.

image of Fig. 1(b). The horizontal axis runs from the center of a pentamer either along ‘A’ or ‘B’ dashed lines. The vertical dashed line in Fig. 3 represents the actual position of the Si nuclei in the pentamer, clearly showing that they do not coincide with positions of the maxima. The lateral bright spot along ‘B’ is more diffuse then the spot close to the central apex along ‘A’. This feature is also observed on the experimental STM images, and that is due to the inclination of a pentamer plane with respect to the surface normal by about $22^\circ$ towards the [116] direction (see Fig. 2).

The observation of spurious images by STM as described above is not limited to the case of pentamers in the (110), (113), (331) surfaces of silicon and germanium. It should be observed virtually on any surface having directional dangling bonds whose axes are not normal to the surface. Of course this will essentially depend on the specific surface bonding and reconstruction details, which can be scrutinized by first-principles atomistic methods.

Establishing a direct connection between the positions of bright spots in STM images and the positions of atomic nuclei can lead to considerable sizing and interpretation errors. For example, the Si surface orientation composed of regularly spaced (111) terraces and triple steps has been erroneously identified. While an early STM study on this subject indicated a
(557) orientation [9.5° off the (111) plane],\textsuperscript{13} latter works including high resolution diffraction data report a (7 7 10) orientation [10.0° off the (111) plane].\textsuperscript{14-19}

In conclusion, we demonstrated that the positions of bright spots in high resolution STM images and the actual coordinates of atomic nuclei may differ substantially. Elusive images can be formed on surfaces having dangling-bond states whose main axis differs from the surface normal, and that may lead to misinterpretation of the experimental data. Pentameric structures on Si(331) observed by STM provided a showcase for the above effect, which if taken into account, reconciles the conflicting theoretical and measured sizes of pentamers occurring on (110), (113) and (331) surfaces of Si and Ge.

**Experimental and computational methods**

The measurements were performed in an ultrahigh vacuum chamber (7 × 10⁻¹¹ Torr) on a system equipped with an Omicron STM. A clean Si(331) surface was prepared by sample flash annealing at 1250°C for 1 min followed by stepwise cooling with 2°C per minute steps within a temperature range 400-850°C. The STM images were recorded at room temperature in the constant-current mode using an electrochemically etched tungsten tip.

Electronic structure calculations were carried using the density-functional plane-wave \textit{VASP} code.\textsuperscript{20-23} The many-body exchange-correlation interactions were accounted for within the semi-local generalized gradient approximation.\textsuperscript{24} Core electrons were replaced by efficient projector-augmented wave (PAW) potentials,\textsuperscript{25,26} allowing a description of the Kohn-Sham valence states using plane-waves with a cut-off energy of 250 eV.

The Si(331)-12 × 1 surface was represented by a periodic slab, consisting of ten atomic bilayers of silicon and 25 Å of vacuum along the surface normal. The bottom side of the slab was passivated by hydrogen atoms, while the top side was prepared according to the 8P-model of the 12 × 1 reconstruction as reported in Ref. 5. Atomic coordinates of the topmost eight bilayers were fully relaxed until the largest Hellmann-Feynman force became smaller.
than 0.015 eV/Å. The electron density (and potential terms) was obtained by sampling the band structure within the Brillouin zone using a $4 \times 4 \times 1$ k-point grid. The local density of states (LDOS) for electrons at the surface was obtained from the Kohn-Sham eigenvalues and eigenfunctions. The STM images were calculated within the Tersoff-Hamann approach, assuming a constant current mode. The WXM software was used to process the experimental and calculated STM images.

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