Seeing the atomic orbitals in STM images of a Si(111)-\((7 \times 7)\) surface

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Abstract. We report on STM studies of a Si(111)-\((7 \times 7)\) surface with subatomic resolution. STM images with double atomic features due to the contribution of two dangling bonds of the silicon apex atom were measured at different bias voltages and tunnelling currents. The results of experiments reveal strong dependence of the subatomic features shapes on the gap resistance and the bias voltage polarity.

The invention of scanning probe microscopy (SPM) [1, 2] allowed surface imaging with atomic resolution. It has been demonstrated recently [3] that the spatial resolution of SPM can be reduced to subatomic scale. The results of ultimately high resolution atomic force microscopy (AFM) experiments [3-5] showed that probing the atom electronic structure with lateral resolution better than 100 pm [5] in AFM is principally possible. The question related to the capability of STM devices to resolve the fine atom electronic structure has been discussed in the literature [4,6-8]. However, only rare scanning tunnelling microscopy (STM) experiments [6, 7, 9] could clearly reveal subatomic structures in the images. In this report we present experimental results demonstrating subatomic features in the STM images of a Si(111)-\((7 \times 7)\) surface. The double features in our STM experiments were better resolved at small tip-surface separations and low bias voltages as it was predicted in pioneering AFM works [3, 4] and more recent calculations and dynamic STM studies [7].

The experiments were carried out in the ultra high vacuum (UHV) chamber of a LAS-3000 spectrometer equipped with room temperature STM (GPI-300). The pressure in the STM chamber was kept below \(1 \times 10^{-10}\) Torr. Si(111) sample (\(p\)-type, 0.3 \(\Omega \cdot \text{cm}\) at 300K) was cleaned using a standard thermal treatment procedure involving a flash heating to 1250\(^\circ\)C and gradual cooling to temperatures below \((1 \times 1) \rightarrow (7 \times 7)\) phase transition. During the flash heating pressure in the UHV chamber did not exceed \(3 \times 10^{-10}\) Torr. The tungsten tips for STM experiments were electrochemically etched in 2M NaOH solution and then sharpened in-situ in UHV by electron beam flash heating and \(\text{Ar}^+\)-sputtering with 600 eV ion beam. Sometimes, before the measurements W tip was brought in a gentle contact with the sample to obtain a silicon terminated apex. This contact remained on the surface a crater with dimensions of several nanometers. STM images of the Si(111)-\((7 \times 7)\) surface presented in Figure 1 were measured in constant current mode with such a silicon terminated W tip.

Figure 1 presents consecutive STM images of the Si(111)-\((7 \times 7)\) surface measured with the same silicon terminated apex at different bias voltages and tunnelling currents. More detail information related to these measurements will be published elsewhere, here we just mention that STM images were taken at various tunnelling parameters to obtain new information about
Figure 1. 15 nm × 15 nm STM images of the Si(111)-(7 × 7) surface measured using a silicon terminated probe. Insets show 8 Å × 8 Å images of the individual adatoms indicated by square frames. STM images were background subtracted and smoothed by 3 × 3 matrix using WSxM software [10].

The fine atom electronic structure visualization in STM experiments. Only several representative examples from a series of successive images are shown in Figure 1. Because of a drift and change of the tip positioning the images in panels (a-i) show not exactly the same surface area.

At larger bias voltages [Figure 1(a)] the STM images demonstrate the adatoms and rest atoms both in the unfaulted and faulted halves. As illustrates Figure 2, the cross-section (1-2) of the image (a) is consistent with the dimer adatom stacking fault model [11]. It was demonstrated in some theoretical calculations [12] that only geometrically perfect single atom terminated STM tips can reveal the rest atoms on the Si(111)-(7 × 7) surface. The sharpness of the tip is also proved by well resolved single atom defects in different images of Figure 1. At negative bias voltages lower than 0.8 V and positive sample biases only the adatom features are resolved [Figure 1(b-i)] that is in accordance with the surface electronic structure [13]. At small negative biases the adatoms are imaged as double protrusions with maxima separated by 2.35–2.5 Å (insets in Figure 1). The splitting of the adatoms is more evident at small negative bias voltages [panels (c,d,g)]. The experimental data also show that the double features are better resolved at larger tunnelling currents at fixed bias voltages of -0.3 V (c,d) and -0.5 V (h,i). The shape of the features changes with decreasing tip-sample separations: almost symmetric double features [Figure 1(c)] become asymmetric at smaller tip-sample distances [Figure 1(g)]. At the smallest positive sample bias voltage measured (0.25 V) some asymmetry of the features can be found though they are not well resolved as double protrusions. At larger positive bias voltages the splitting of the atomic features is not so well resolved [Figure 1(f)].

The shapes of the double features at low negative bias voltages [Figure 1(g)] are qualitatively similar to ones measured in the high resolution AFM experiments [3]. Thorough theoretical
and experimental studies [3, 4, 14] showed that the double features in the Si(111)-(7 × 7) AFM images can be explained by contribution of two Si(001) tip sp$^3$ dangling bonds imaging twice one Si adatom on the surface. Moreover, the results of the charge density calculations for the Si(001) tip - Si(111)-(7 × 7) surface system [4] showed that similar features can be observed in STM experiments at small tip-sample separations (about 4 Å and below). We suggest that this situation takes place in our STM experiments with silicon terminated apex. Note also that the distances between two maxima of the double features in Figure 1 are also consistent with results of the AFM experiments [3] and charge density calculations [4].

A comparison of the images in Figure 1 shows that asymmetry in the double features becomes more substantial when the gap resistance (tip-surface separation) decreases. At the smallest tip-surface distances the adatoms are resolved as one larger (from the left side) and one smaller (right side) protrusions while at larger distances both protrusions are comparable in size (see insets in Figure 1). Remarkably, similar asymmetry of the double features was observed in the AFM experiments and explained by an apex atom relaxation opposite to the scan direction [3, 4] as schematically shown in Figure 2(b). At small distances, that are necessary for atomic orbital imaging, a chemical interaction can modify STM images substantially [15]. In this case the observed asymmetry effect can be caused by a chemical bonding of the adatom and tip apex atom. Since the adatom can form a bond to only one of the tip dangling bonds at the same time, a slight elastic deformation may be favorable than breaking one bond and formation of another one. In this case the first of the tip orbitals can form a bond with the surface adatom longer than the second orbital thus inducing two nonequivalent subatomic features in the STM images. That is especially pronounced in Figure 1(g).

In some experiments STM images demonstrating double features with other orientations were measured [Figure 3(a)]. Despite some relative rotation of the double features determined by the silicon apex geometry, the distances between the double maxima in Figures 1 and 3 are in a good agreement. Note that sometimes silicon terminated tips produced images with multiple atomic features as shown, for example, in Figure 3(b). As can be seen in the middle part of this picture, after some occasional change of the tunnelling conditions the adatoms are imaged as multiple protrusions though surface defects are well resolved. In several experiments with clean ion-etched W tips we could also measure images with split atomic features. Appearance of the subatomic features in experiments with ion-sputtered W tips may be explained by catching Si atoms from the surface [16, 17] or fine electronic structure of the tungsten probe [5].

The STM images presented in Figures 1 and 3(a,b) reveal the same splitting of all atomic features within the measured frames. That allowed us to suggest some kinds of “multiple-tip” effects where individual atomic orbitals associated with a silicon atom at the apex produce the apparent atom splitting. Note that possibility of two or three apexes shifted by approximately 2.5 Å plus (7 × 7) lattice vector is not supported by well resolved surface defects which are not reproduced in other parts of the images (Figure 1 and large area scans not shown here). A blunt tip with two atoms at the apex separated by 2.35–2.5 Å can also be excluded as a reason of the double features in Figure 1. One can see well resolved adatom and rest atom protrusions in the image taken at a sample bias of -1.4 V [Figure 1(a)] that is only possible with geometrically perfect tips [12]. Furthermore, blunt tips, mostly, produced additional features in the corner holes at low tip-sample distances and non-contrast images at large bias voltages (above 1.0 V) that is not seen in this case. On the contrary, the experimental situation when the corner holes and the double adatom features are clearly resolved (Figure 1) is rather infrequent. The tips which allow to measure such images, statistically, are very unstable that also indirectly prove their sharpness.

In some experiments with ion-sputtered W tips at small bias voltages (and tip-surface separations) we could resolve images similar to presented in Figure 3(c). Note that the same tip at larger bias voltages demonstrated well resolved Si(111)-(7 × 7) STM images with single
Figure 3. STM images of the Si(111)-(7×7) surface measured in different experiments with silicon (a, b) and tungsten (c) terminated probe. (a) 9 × 9 nm², $V = -0.8$ V, $I = 0.07$ nA; (b) 14 × 14 nm², $V = 0.5$ V, $I = 0.1$ nA; (c) 6.5 × 6.5 nm², $V = 0.1$ V, $I = 0.06$ nA

spherically symmetric atomic features. One can also see a single atom defect in the image shown in Figure 3(c) proving the quality of the used W tip. In this image the double features corresponding to nonequivalent adatoms are rotated. This indicates that multiple protrusions in that case reflect some details of fine electronic structure of the surface or appearance of new tunnelling channels at small distances. Detail explanation of the images presented in Figure 3(b,c) demands additional experimental and theoretical studies though the presented data demonstrate that STM with suitable tips and optimized tunnelling parameters, probably, can be used for probing specific electron states associated with the surface atoms rather than with the tip apex atom.

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