Local force gradients on Si(111) during simultaneous scanning tunneling/atomic force microscopy

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The authors report simultaneous scanning tunneling and force imaging of Si(111) 7×7 with sub-angstrom oscillation amplitudes. Both constant height and constant current scans with tungsten tips/levers always showed larger attractive stiffness over corner holes than over adatoms, the opposite of theoretical expectations. Constant height scans show that this cannot be explained by interaction of tip motion with long range forces. Silicon levers, however, sometimes exhibited inversions of force contrast following local tip changes. The authors suggest that there may be charge variations between atomic sites on the surface, which produce electrostatic tip forces additional to the covalent forces usually regarded as dominant. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2717115]

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been very powerful tools in surface science with their capability of both atomic resolution imaging and spectroscopy. On surfaces having some conductivity, the combined use of the two techniques is of great interest because forces and tunnel currents, and their associated spectroscopies, give complementary data. This is important for attempts to chemically or structurally identify individual species or adsorbates on surfaces or in nanostructures. The power of collaborative use of noncontact-AFM (nc-AFM) and STM has been shown for Ge/Si(105).[1] However, truly simultaneous measurement of forces and tunnel currents is a more demanding task. With large lever oscillation amplitudes the tip is in tunneling range only during a very small fraction of the cycle, so time and separation averaged current is measured. It is highly desirable to do STM and AFM at the same time (pixel for pixel) because there is then no uncertainty about registry of images taken at different times, or about possible changes of surface or tip between images. Simultaneous measurements as close as possible to true STM mode are best accomplished using sub-angstrom oscillation amplitudes.[2,3]

The Si(111) 7×7 surface has been studied by many groups using standard nc-AFM methods ever since the first true atomic resolution images reported by Giessibl.[4] We have previously presented some limited AFM/STM results using sub-angstrom oscillation amplitudes.[2] In this letter we report new results using a system with greatly improved force resolution. A commercial UHV AFM was modified to incorporate a Fabry-Pérot fiber interferometer to achieve high sensitivity to lever deflection.[5] Power fluctuations of the laser diode, previously problematic, were suppressed by adding a rf modulation to the dc input of the laser driver.[6] This minimizes the influence of back reflections into the laser diode by decreasing the coherence length. Along with a better choice of laser diodes and additional components such as optical isolators, this resulted in about an order of magnitude enhancement in signal to noise compared to our previous design.[5] The sensitivity of $\sim 2\times10^{-4}$ Å/$\sqrt{\text{Hz}}$ enables routine and easy measurement of the force gradient interactions between the tip and the sample and also enables simultaneous measurement of tunnel current, tunnel barrier height, and energy loss.[3,5,7]

The lever is oscillated with ultrasmall amplitudes (0.25–0.5 Å) at a frequency well below its resonance. Changes in the oscillation amplitude due to force interaction are recorded using a lock-in amplifier. The force gradient interaction between tip and sample can be expressed as

$$dF/dz = k_0(1 - A_0/A),$$

where k_0 is the lever stiffness, A_0 the free oscillation amplitude (i.e., far from surface), and A the measured amplitude with tip-surface interaction present.[8] The deconvolution or model assumptions in large amplitude resonance techniques are not required. The energy input to the interacting tip-sample system is very low, and the perturbation is minimal in probing the interactions. During raster scanning, the feedback loop response time is slower than the oscillation period, so that regular STM can be performed and simultaneously the tunnel barrier height determined from the small resulting oscillation in current.[3,7] Both commercial silicon cantilevers and homemade tungsten cantilevers were used, with spring constants of about 40 and 230 N/m respectively. The spring constant was calibrated directly using a nanoindenter and was also calculated from geometry and thermal oscillation measurements. The Si(111) sample was cut from P-doped, n-type wafer with 0.7–0.9 Ω cm resistivity, oriented to within 0.20° of (111) plane. It was cleaned by flash annealing to 900 and 1100 °C for a few tens of seconds following an overnight degas at about 600 °C.

Figure 1 shows STM and force gradient images taken simultaneously with an oscillation amplitude A_0 of 0.3 Å. Both STM and force gradient reveal the 7×7 structure with atomic resolution. The darker shading in force gradient images indicates more negative interaction stiffness, that is, higher attractive stiffness. The force gradient corrugation from adatom to corner hole is about 2 N/m and, crucially, the corner holes show larger attractive force gradient. This surprising result is opposite to most reported nc-AFM experiments. Our technique is not directly comparable to large amplitude nc-AFM which measures the frequency shift, which is effectively an integral of force gradient over the

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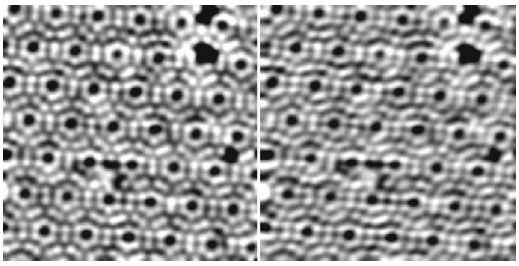

FIG. 1. Simultaneous STM (left) and force gradient (right) images of Si(111) 7×7. Image size of 150×150 Å^2, $V_{tip}=2$ V, $I_T=0.25$ nA, $A_0=0.3$ Å, and $k_0=40$ N/m. Darker shading in force gradient indicates more negative values of the interaction stiffness. Vertical (B-W) scale in force gradient (FG) is 3.3 N/m.

whole oscillation cycle. Nonetheless, theoretical modeling[9] of tip-sample interaction force gradients on Si(111) also suggest the opposite contrast to what we observe here. We note that the calculations consider a tip having only a covalent interaction with the surface and a van der Waals (vdW) type background. Interestingly, in some reported large amplitude AFM experiments the observed contrast was similar to ours in Fig. 1, that is, inverted from the expected. For instance, Guggisberg *et al.*[10] acquired frequency shift images of the surface using tunnel current feedback and the corner holes showed more negative frequency shift than other sites, which suggests a more attractive force gradient. Hasegawa and Eguchi[11] reported similar results from STM/AFM experiments using relatively large oscillation amplitudes. Understanding of their contrast inversion is lacking. We shall see that tip composition may be significant.

The calculations of Perez *et al.* used a constant height contour for the tip, whereas in the experiments of Fig. 1 the tip height is moved to maintain the tunnel current constant. In an earlier paper[2] we suggested that this vertical motion of the tip could explain the force gradient contrast inversion. The motion of the tip towards a corner hole as the raster scan goes over the hole actually causes an increased attractive force gradient from the vdW background, which could explain the images. However, this requires quite a large vdW or long range term for the suggested explanation to be valid. We now have a very large number of images with tungsten levers, having various vdW radii (determined by the method described in Ref. 12), but we always obtain the same contrast, i.e., corner holes show larger attractive force gradient than adatoms and restatoms. One way to be certain about a long range force effect is to image at constant tip height, eliminating the macroscopic tip motion. We have now done this by regulating the tip-sample distance in one scan direction with tunnel current feedback on and then turning the feedback loop off in the reverse scan direction. STM topography (i.e., tip vertical motion), tunnel current, and force gradient were all simultaneously recorded during both direction scans. This allowed us to compare the force gradient contrast in constant current and constant height modes within a single scan (see Fig. 2). The 7×7 structure is seen in STM topography in the forward scan and in the tunnel current in the backward scan. The force gradient exhibited atomic resolution in both directions, interestingly with the same sign of contrast. In no such dual mode scans with W tips did we ever observe an inversion of force gradient image between constant current and constant height modes—the corner holes always appear with larger attractive force gradient than adatoms. In Fig. 2 the corner hole-adatom force gradient contrast was 1.4 N/m in constant height, and 1.2 N/m in constant current scans. There is obviously some effect of long range force terms, but it is small, and cannot account for the main atom-resolved contrast.

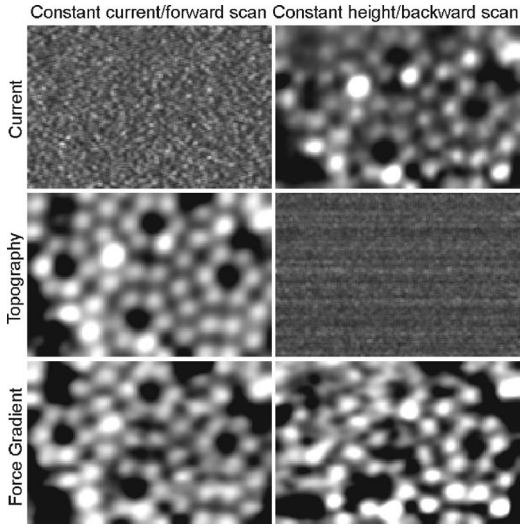

FIG. 2. Simultaneous height, current, and force gradient, taken at 0.5 nA constant current in forward scan direction and constant height in reverse scan direction. W cantilever, $V_{tip}=2$ V, $A_0=0.5$ Å, and $k_0=231$ N/m. Darker shading in force gradient indicates more negative values of the interaction stiffness. Vertical (B-W) scale in both directions of ~1.85 N/m.

Another possible explanation could be that during imaging the tip is close enough to the adatoms for their interaction with the tip to be in part repulsive, and thus less overall attractive, while the corner hole-tip interaction remains purely attractive. To investigate this possibility we made numerous measurements of force gradient and tunnel current versus separation, using the same lever. Such force gradient-distance "spectroscopy" shows the long range vdW and electrostatic terms as well as short range interactions (Fig. 3).[12,13] The attractive maximum in total force gradient corresponds to tunnel current values of about 5 nA. Although these curves are not site specific, it is likely that some were over adatoms, yet we did not observe any evidence of repulsion at currents much below 5 nA. The tunnel current values used in the typical imaging scans are, however, far below 5 nA. More direct evidence comes from increasing the tunnel current between two images, from 0.25 to 5 nA. This increased both the force gradient contrast magnitude, with the same contrast polarity, and also increased the overall oscillation

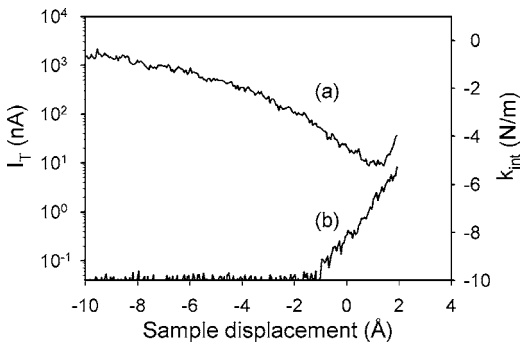

FIG. 3. (a) Total interaction stiffness and (b) tunnel current measured as a function of tip-sample displacement. W cantilever, $A_0=0.5$ Å, and $k_0=231$ N/m. Average of four curves across surface.

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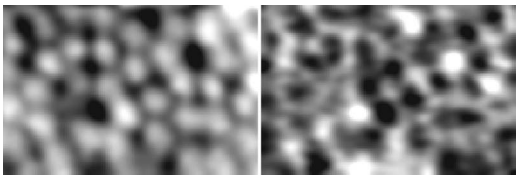

FIG. 4. Simultaneous STM (left) and force gradient (right) of Si(111) 7×7. $V_{tip}=2$ V, $I_T=0.25$ nA, and $k_0=40$ N/m. (a) Image size of 60×40 Å^2. $A_0=0.25$ Å. Vertical scales of 0.92 N/m (FG) and 2.6 Å (STM).

amplitude. This behavior would not be possible if any part of the image at 0.25 nA were in repulsion, that is, closer than in the attraction maximum. It seems unlikely that repulsion at adatom sites can wholly explain the image contrast we observe.

An important insight into the possible interaction mechanism came from using silicon rather than tungsten lever/tips. Si tips are used in most nc-AFM experiments in the literature. We found that Si tips generally gave similar force gradient contrast to W tips, but sometimes after a tip change (to what we will call tip type B, which occurred for about 15% of imaging with Si tips) the force gradient contrast was inverted, as shown in Fig. 4. Note that the STM topographic contrast remains normal—there is no wholesale change in tip motion pattern as a result of the tip change, yet the force gradients now show stronger attractive force gradient at the adatoms than corner holes. This result strongly suggests that the chemical species of atom at the tip apex matters a great deal for the forces present. Changing the tip atom can invert the force gradient while retaining normal STM currents. The obvious candidate for this behavior is a change of charge polarity at the tip, along with significant electrostatic interaction force between tip and surface. Recent calculations and experiments on TiO_2 suggest this is indeed possible.[14–16] Our results therefore also imply that there may be significant, and in principle now measurable, variation of charge or potential between individual atomic sites on the silicon surface.

There are good reasons to believe this interaction is highly localized. We observed that the force gradient corrugation in simultaneous STM/AFM scans (for all tips) did not exhibit a particularly pronounced voltage bias dependence; applied voltage just provided the usual parabolic long range term.[10] The electrostatic force from the applied voltage between tip and sample cannot be contributing significantly to the local contrast in force gradient. We emphasize that tip type B inversions in contrast took place only with Si tips, never with W tips. Clearly, the chemical species at the tip apex has a very significant role in force gradient contrast. Adatoms such as oxygen, when adsorbed onto Si tips, are more likely to affect local tip charge than when adsorbed onto metallic tips such as W. It is interesting that we can obtain normal STM images even when the force gradient images completely invert, and perhaps not wholly surprising given STM dependence on density of states (DOS) rather than electrostatics. It also suggests that force induced tip relaxations, which can affect STM images[17,18] cannot be the whole explanation for the surprising local force gradient contrasts we observe.

Our results suggest that localized electrostatic forces at surfaces might be significant even for pure Si(111). It is clear that long range forces cannot explain the unexpected contrast polarity. Tip changes are a traditional concern in scanning probe microscopy, and are problematic for theoretical modeling—images which do not show expected contrast are often left unpublished. In this case [and as recently shown for TiO_2 (Ref. 14 and 16)] tip changes reveal processes which could be important for understanding imaging. Since STM senses DOS, and AFM senses force, with the same topography and composition when simultaneous, combining them should give more information about surface structure and species than either technique in isolation.

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