High Resolution Atomic Force Microscopic Imaging of the Si(111)-(7 × 7) Surface: Contribution of Short-Range Force to the Images

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Observation of the rest-atom layer of the Si(111)-(7 × 7) surface is performed by atomic force microscopy. By detecting the force due to the single chemical covalent bond formed between the tip and the sample surface, individual atoms on the layer were clearly resolved. Unprecedented high spatial resolution was achieved by setting the detection force at a small value and by reducing background forces due to the long-range interactions with the small oscillation amplitude of the cantilever and sharp probe tip.

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Atomic force microscopy (AFM) [1] is used in many fields to observe nanoscale structures on surfaces because of its wide versatility regardless of the electrical conductance of the sample. It uses the force acting between atoms as a probe. The atomic force, in the case of silicon surfaces the force due to the formation of the chemical covalent bonding between the apex atom of the probe tip and the surface atom, is highly sensitive to the probe-sample distance similar to the tunneling current of scanning tunneling microscopy (STM). The chemical covalent bond is formed at a very proximate distance between the atoms (< 0.5 nm), and its force decays steeply with distance (by a factor of 4 per 0.1 nm in Si-Si bonding) [2]. Thus, it works as a local proximate probe with the advantage of versatility to insulating materials. Recent developments in force detection techniques, in particular, introduction of the frequency modulation (FM) detection technique [3], have made it possible to detect the atomic force and obtain adatom-resolved images of the Si(111)-(7 × 7) surface [4–6]. Compared with STM, however, spatial resolution remains limited. For instance, observation of rest atoms, which are located on a plane below the adatoms by 0.10 nm, has not been reported except by Lantz *et al.* [7] at the temperature of liquid helium (7.2 K) [8].

To improve the spatial resolution and stability of the observation, it is necessary to set the minimum force acting on the tip to avoid the unwanted atom diffusion/transfer over the tip surface or between the tip and sample. Reducing background forces due to long-range atomic interactions, such as van der Waals (vdW) force, is also crucial to improving the resolution since long-range forces, which by nature do not have atomic-scale spatial sensitivity, tend to smear the high sensitivity of the short-range chemical force and thus deteriorate the spatial resolution. This study demonstrates that, with careful pretreatment of the cantilever and appropriate experimental parameters, the structure of the rest-atom layer can be imaged using AFM by detecting the short-range force due to single chemical bonding. The detection of the short-range force is verified by analysis of the frequency shift versus distance curve (force curve). The curves show a steep drop of the frequency shift at proximate distance, quantitatively consistent with results of a theoretical study with a model silicon surface [2].

In the present study, we used an ultrahigh vacuum (UHV) Omicron UHV system, which adopts a beam reflection method for detecting cantilever deflection. In order to improve sensitivity to the deflection, the originally attached light-emitting diode was replaced with a laser diode. Base pressure is 3×10^{-9} Pa. As a sample, a piece of Si(111) wafer (As doped, n-type, 1–3 mΩ cm) was loaded into the UHV chamber and flashed at 1200 °C after an outgas to make the 7 × 7 surface. During the observation, the tip and the sample were kept at room temperature. We used Nanosurf products as the AFM control system, such as an automatic gain controller to maintain the resonance oscillation of the cantilever at a constant amplitude, and an FM demodulator to obtain the frequency shift. A commercially available cantilever made of silicon (Nanosensors) was used as the probe. Before using it for imaging, the cantilever was annealed *in situ* above 900 °C by electron-beam bombardment to remove the native silicon oxide layer covering the tip and to improve the Q factor.

Figure 1(a) shows an AFM image taken on the Si(111)-(7 × 7) surface using the above-mentioned method. When taking the images, the frequency shift Δf was maintained constant at -20 Hz. The oscillation amplitude A_0 measured at the tip position was set at 2.8 nm, which is small compared with other experiments [9]. A bias voltage of $+0.20$ V was applied to the sample to minimize the effect of the electrostatic force between the tip and the sample. The normalized frequency shift $\gamma = \Delta f k A_0^{3/2}/f_0$ (described in Ref. [10]) is -0.46 fN m$^{1/2}$ in the condition, which is also quite small compared with other experiments [9], indicative of the small force on the tip.

According to the established structural model of the 7 × 7 surface, the dimer-adatom-stacking fault (DAS) model proposed by Takayanagi *et al.* [11] depicted in

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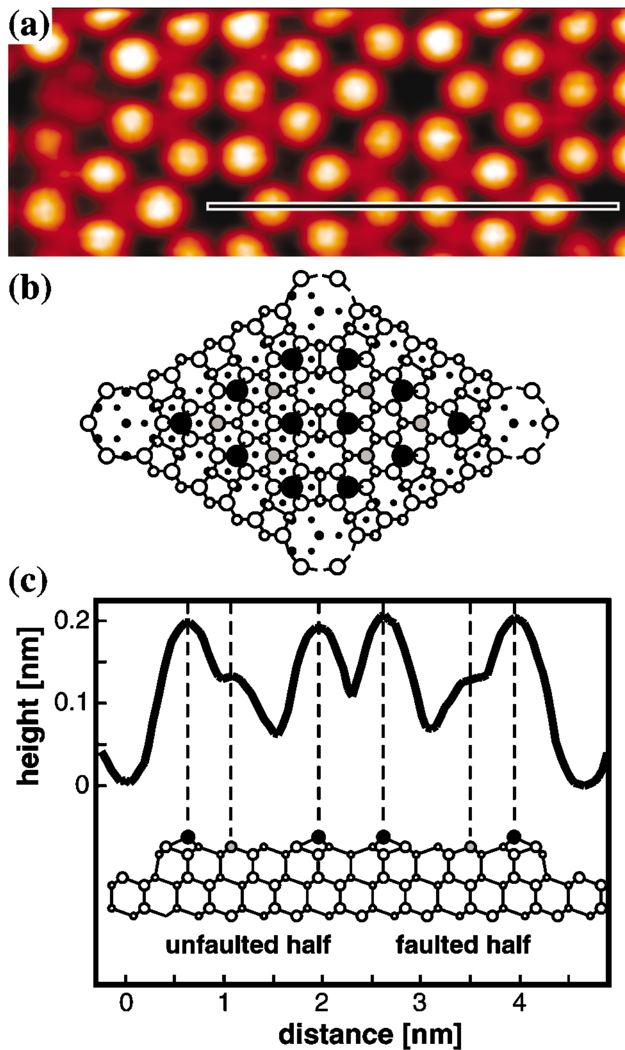

FIG. 1 (color). (a) An atomically resolved AFM image of the Si(111)-(7×7) surface. The observed area of the AFM image is 7.5 nm × 3.0 nm. The resonance frequency f_0, spring constant k, and Q factor of the cantilever are 298 009 Hz, 46 N/m, and 54 200, respectively. (b) Top view of the DAS structural model of the Si(111)-(7×7) surface. (c) A cross-sectional plot measured on the long diagonal line of the 7×7 unit cell drawn in (b), together with a side view of the DAS structural model, demonstrating a precise fitting of adatom and rest-atom positions.

Fig. 1(b), the adatoms (filled circles in the ball-stick model) have a dangling bond and thus are capable of forming a covalent bond with an atom on the tip to make a contrast in AFM images. A dangling bond is also located on rest atoms [shaded circles in Fig. 1(b)]. The AFM image, shown in Fig. 1(a), obviously shows bright features at the rest-atom sites. In a cross-sectional line plot taken along the long diagonal direction of the unit cell [Fig. 1(c)], hump features are clearly resolved at the sites corresponding to the rest atoms. Note that the peak positions of the humps are located exactly in the positions where the rest atoms should be, as is demonstrated by a vertical comparison of the cross-sectional plot and a side view of the structural model.

In reported AFM images of the Si(111)-(7 × 7) structure, adatoms are frequently contrasted like a half sphere regularly arranged on a plane, making an image resembling the reverse side of a muffin tin [7,12]. This is presumably due to the vdW background force. Being a long-range force, the vdW force varies gradually with the distance independent of the local atomic site. Since the vdW force becomes stronger in the depleted sites on the surface, it can dominate the detected force and prevent the tip from moving further under the condition of constant force, creating the depleted area flat in the AFM image. With the background force overlapped, even in the area where the image is not flat, the apparent depth of the dip structure becomes shallower than the actual depth.

Compared with the images mentioned above, the image shown in Fig. 1(a) has many features reproducing the real atomic structure of the surface, as observed by STM. Careful inspection of the images reveals that individual atoms in the second layer, which are separated by 0.38 nm, are also resolved in the area where adatoms are missing, as shown in Fig. 2(a). In Fig. 2(b), a structural model is overlapped with the image, demonstrating registry matching between the image and the model. The height difference of the hump features due to the rest atoms from the adatoms is about 0.08 nm, which is slightly smaller than the structural height difference (0.10 nm). A first-principles calculation by Pérez *et al.* [2], who studied the properties of forces acting between a model Si tip and the Si(111)-(5 × 5) surface structure, indicates that potential and force profiles due to the Si-Si chemical bonding perpendicular to the surface do not change over the adatom and rest-atom sites. Their calculation includes the effect of lattice relaxation. Thus, the theory predicts that the observed height difference should not differ from the structural one. Our result indicates a small overlap of the background force, as discussed in more detail in analysis of the force curve.

So far, the importance of reducing the long-range force acting on the tip compared to the short-range force has been discussed. The force curve, the spectrum of frequency shift Δf as a function of the tip-sample distance s, provides information on the characteristics of the force.

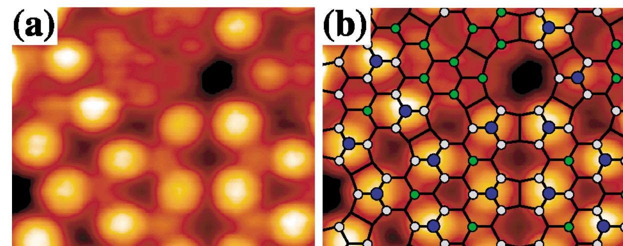

FIG. 2 (color). (a) An AFM image of the Si(111)-(7 × 7) surface showing individual atoms in the rest-atom layer. The observed area is 3.8 nm × 3.0 nm. Experimental parameters are the same as those shown in Fig. 1(a). (b) A structural model is overlapped with the AFM image (a).

Figure 3 shows the force curve we measured on the 7×7 surface. Two kinds of forces are considered in interpretation of the force curve: the short-range chemical force and the long-range vdW force. Electrostatic force can be disregarded since we compensated for it by applying an appropriate bias voltage to the sample.

For analysis of the force curve, a large amplitude approximation [10] was used to obtain the curve from an analytical form of the force profile. However, the approximation was not appropriate for the vdW force in our experimental conditions because of the small oscillation amplitude of the cantilever. Under these conditions, the approximation overestimates the value of frequency shift Δf by more than 50% at a distance where the long-range force is dominant (1 nm $< s <$ 5 nm) [14]. For this reason, discussion using the normalized frequency shift γ is inappropriate in a quantitative interpretation of our study. We thus used an analytical formula to describe the frequency shift due to the long-range force [15,16] and found that a tip that is either a conical or parabolic shape, which has been used for fitting, does not fit well with the curves we obtained. A tip with a sharp point at its apex [17] showed a remarkable fit to the experimental curve at the relevant distance, as demonstrated in Fig. 3. In an inset of Fig. 3, tip model *A* used in our analysis is shown together with a side-view model of the DAS structure. A tip model used for fitting in another work [13] is depicted in B, showing remarkable contrast with tip *A*. Here, we do not intend to claim that the shape of the tip we used in our study is like that shown in the inset (tip *A*). We can, however, definitely conclude that the background component due to the long-range force is obviously reduced because of the tip shape. As a reference, a simulated vdW force curve with tip *B* is drawn with a dashed line in Fig. 3.

For a fitting of the chemical bonding force, a Morse potential was assumed, as suggested by Pérez *et al.* [2]. The parameters for describing the potential, such as binding energy and the decay length, were fixed to the value estimated in their analysis. We confirmed by numerical analysis that the large amplitude approximation is applicable for the chemical force since the force works only in a short range, and we used the approximation in our fitting. Taking two fitting parameters, the coefficient χ, which determines the tip shape (see Ref. [15]), and the distance between the origins of the short-range and long-range forces, we obtained a curve in good agreement with the experimental one in a whole range (see Fig. 3). The steep drop of Δf in the range of the tip-sample distance of 0.6 nm $< s <$ 0.8 nm, in addition to the highly resolved imaging shown in Figs. 1 and 2, implies that the measured Δf at the proximate distances ($<$ 0.8 nm) is due to the single chemical bonding between the silicon atoms on the tip and the sample surfaces. We found that the decay length of the frequency shift agrees quantitatively with the theoretically estimated value [2].

Highly resolved AFM images with a quality comparable with STM can be taken under appropriate experimental conditions. One of the conditions is a small force to prevent the atom diffusion/transfer over the tip surface or between the tip and the sample. In the condition in which the images shown in Figs. 1 and 2 were taken, for instance, the short-range chemical force is calculated to be 0.02 nN, which is roughly 1 order smaller than other experiments (e.g., Ref. [13]). To detect a small short-range force, we need to reduce the background component originating from the long-range force. Since Δf is calculated by the integration of the force in the cycle of the cantilever oscillation, a small amplitude of the oscillation enhances the relative ratio of the short-range component over the long-range force [18]. We therefore set the oscillation amplitude to a rather small value (2.8 nm). Using a sharp tip protruding such as the one shown in inset (A) of Fig. 3 is crucial for reducing the background and thus detecting the short-range force.

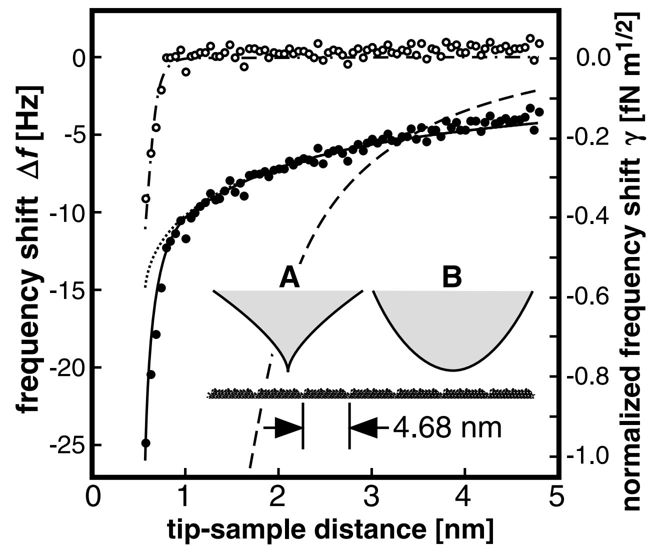

FIG. 3. A frequency shift Δf versus tip-sample distance s curve (force curve) measured on the Si(111)-(7×7) surface. Experimental parameters for making the curve are as follows; $f_0 = 298021$ Hz, $k = 46$ N/m, and $A_0 = 4.0$ nm. Experimental data points are marked with a filled circle. The fitted line is drawn with a solid line. A dotted line depicts a component by the long-range vdW force, and an open circle shows the experimental data points minus the component of the long-range force. The dash-dotted line is a component due to the short-range chemical force. The sum of the dotted line and dash-dotted line should be equal to the solid fitted line. Inset: Model tip shape deduced from the fitting depicted with a side view of the surface structural model. Model *A* is fitted nicely with our experimental data and model *B*, a parabolic shape with an apex radius of 4 nm, is the one used for fitting to the data in Ref. [13]. A simulated long-range force curve with tip *B* is drawn in the plot (dashed line), demonstrating a strong reduction of the background using tip *A*.

To reduce the background by the long-range force, as mentioned above, the oscillation amplitude A_0 was set at a small value. The small oscillation amplitude itself, however, deteriorates the signal-to-noise ratio in an output of the FM demodulator. Two noise components contributed

to the noise in our experiments; one is due to a thermally activated random oscillation $\delta f_{\rm th}$ and the other is due to electrical noise in an input of the FM demodulator $\delta f_{\rm el}$, mostly coming from current amplifiers that convert the current signal of the photodiode detector to voltage. Total noise is given by $(\delta f_{\rm th}^2 + \delta f_{\rm el}^2)^{1/2}$ since they are independent. $\delta f_{\rm th}$, inversely proportional to A_0, is written $(f_0 k_B T B / 2\pi k Q)^{1/2}/A_0$, where k_B, T, and B are the Boltzmann constant, temperature, and bandwidth of the demodulator, respectively [3]. $\delta f_{\rm el}$ is also in inverse proportion to A_0, described as $(2B^3/3B')^{1/2}(a_0/A_0 2\pi)$, where a_0/A_0 is a ratio of the noise to the oscillation amplitude measured with a bandwidth of B' [19]. Under our experimental conditions, both contributions are comparable around 0.1 Hz. According to these formulas, increasing the Q factor of the cantilever is effective in reducing the thermal noise under the condition of fixed temperature T and oscillation amplitude A_0.

Appropriate treatment is necessary to maintain a sharp tip on the cantilever and improve its Q factor. Various pretreatment methods for commercial cantilevers have been used so far, e.g., moderate-temperature annealing, usually lower than 200 °C, intending to remove contamination layers such as water on the silicon tip, and/or sputtering with argon ion to remove the silicon oxide layer that naturally formed in the cantilever production process. Using transmission electron microscopy, we characterized the tip shape and found appropriate annealing to be around 900 °C, high enough to remove the oxide layer on the tip. Since moderate annealing does not remove the native oxide layer, the tip has to contact the surface before the bare silicon layer is exposed. However, this contact may blunt the tip unless the tip position is controlled very carefully. The sputtering obviously blunts the tip, too. Compared with those treatments, the high temperature annealing above the temperature of the silicon oxide desorption is ideal for making a clean, bare tip without blunting.

The Q factor can also be improved by high temperature annealing. In a typical case, while the Q factor of the cantilever was about 9100 without the annealing, by annealing at 400 °C it improved to 17 000. After high temperature annealing at 900 °C, it further improved to 60 900. The improvement is presumably due to the oxide layer removal as reported by Yang *et al.* [20]. High temperature annealing is quite effective in maintaining a sharp tip, good for reducing the background component and, thus, enhancing the short-range force, and reducing the thermal noise by improvement of the Q factor.

This Letter presents observation of rest-atom and second-layer atom resolved AFM images. Using a small force setting and a small oscillation amplitude of the cantilever, we succeeded in detecting the force due to the single chemical covalent bond acting between the atoms on the probing tip and sample surfaces. High temperature annealing of the tip assists in obtaining a bare silicon tip on the cantilever without unwanted tip blunting and improving the Q factor of the cantilever. The capability of AFM for taking highly resolved images comparable with STM opens up the versatility of the technique for practical applications.

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