Imaging of all Dangling Bonds and their Potential on the Ge/Si(105) Surface by Noncontact Atomic Force Microscopy

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High-resolution noncontact atomic force microscope (AFM) images were successfully taken on the Ge(105)-(1 × 2) structure formed on the Si(105) substrate and revealed all dangling bonds of the surface regardless of their electronic situation, surpassing scanning tunneling microscopy, whose images strongly deviated from the atomic structure by the electronic states involved. An atomically resolved electrostatic potential profile by a Kelvin-probe method with AFM shows potential variations among the dangling bond states, directly observing a charge transfer between them. These results clearly demonstrate that high-resolution noncontact AFM with a Kelvin-probe method is an ideal tool for analysis of atomic structures and electronic properties of surfaces.

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Scanning tunneling microscopy (STM) [1] has been utilized to determine surface atomic structure with atomically resolved images. Probing surface electronic states near the Fermi energy (E_F) [2], STM images, however, does not necessarily represent the atomic structure of surfaces. On the other hand, atomic force microscopy (AFM) [3] probes the force acting between the tip and the sample surface. It is believed that AFM provides us with surface topographic images without being disturbed by the electronic states. So far, because of limited spatial resolution, this unique performance of AFM has not been demonstrated. Moreover, using a Kelvin-probe method [4,5], AFM can also allow us a mapping of surface electrostatic potential in high spatial resolution. Its application to an atomically resolved potential profile is, however, hampered again by the limited resolution.

In this Letter, we demonstrate that high-resolution AFM can reveal true images representing the atom positions on a surface where STM is influenced greatly by the electronic effect. In addition, using the Kelvin-probe force microscopy (KFM) we show images of potential variation on all surface atoms, directly monitoring a charge transfer among the dangling bond states. These images demonstrate that high-resolution noncontact AFM (NC-AFM) is an ideal tool for analysis of atomic structures and electronic properties of surfaces.

The first true atomically resolved AFM images were achieved by Giessibl [6] with a frequency demodulation method. Then its spatial resolution was improved to a level comparable to or better than that of STM, for instance, resolving the rest atoms [7,8] and adatom imaging in the subatmoic resolution [9] of the Si(111)-(7 × 7) structure, by detecting a force due to a single chemical bonding between dangling bonds of the tip apex and sample atoms [10,11]. These works were, however, performed on the surface whose atomic and electronic structures are well established, mainly with a purpose of revealing imaging mechanisms of AFM. While the STM images taken on the surface basically represent its atomic structure, the superior performances of AFM for structural analysis were not demonstrated in these studies.

A Ge(105)-(1 × 2) surface grown on the Si(105) substrate is used to examine the performance of NC-AFM. The surface has been studied as a facet surface of Ge "hut" cluster epitaxially grown on the Si(001) substrate [12]. Recent studies by STM and first-principles calculation found that the electronic effect strongly affects STM imaging on this surface [13–15]. Being a vicinal surface tilted by 11.3° from a (001) plane; basic entities on the (105) surface are dimer structures arranged on narrow terraces with a width of a few nanometers (Fig. 1). The currently accepted atomic structure of the surface is called rebonded step (RS) model, as shown in Fig. 1 [13–15]. A normal dimer is located in the upper terrace of the type-B (001) step (colored orange with C and D atoms in Fig. 1). Atoms in the lower terrace (colored yellow with A and B atoms) are rebonded with the step-edge atoms to reduce the number of the dangling bonds into eight per unit cell. Four types of dangling

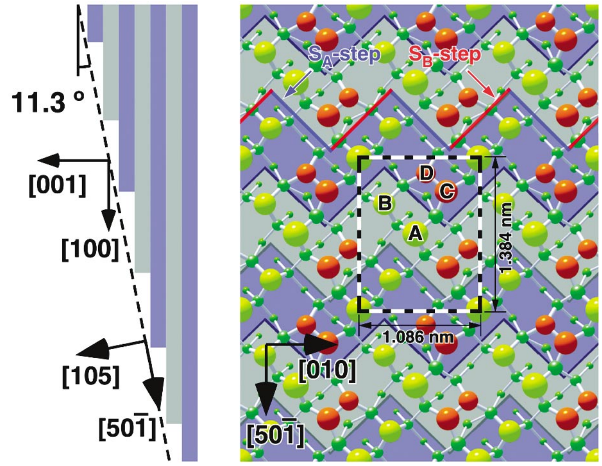

FIG. 1 (color). Rebonded step (RS) model of the Ge(105)-(1×2) surface by a first-principles calculation including an effect of the lattice mismatch with the substrate [14]. The unit cell is indicated by a rectangle on the model. The size of a ball reflects the vertical height of the atom.

bonds, marked A, B, C, and D, are on the surface structure [16].

The experiments were done by an ultrahigh vacuum (UHV) AFM-STM system (Omicron) along with a commercial frequency demodulator and automatic gain controller (Nanosurf). Base pressure of the vacuum is 3.0×10^{-9} Pa. A commercially available Si cantilever (Nanosensors) was used as an AFM probe. For the KFM measurement, we used a commercial Si cantilever with a W-tip sharpened by a focused ion beam (FIB) technique [17]. Before AFM observations, both types of cantilevers were annealed *in situ* above 900 °C by an electron bombardment method to remove the oxide layer covering the tip and to improve a Q factor of the cantilever [7]. The Si(105) substrate was outgased around 600 °C and cleaned by flashing at 1300 °C. Subsequently, germanium was deposited from a solid Ge source with the substrate temperature held at 400 °C [13]. The deposition rate and amount of Ge were calibrated using a quartz thickness monitor and a typical rate and amount were 0.5 ML/ min and 6 ML, respectively. After the deposition, the sample was annealed at 400 °C for 10 min and cooled gradually to room temperature. All STM-AFM measurements were done at room temperature.

To our AFM system we incorporated a potential measurement unit for KFM. When an electrical potential of the AFM tip is not balanced out with that of the sample, an electrostatic force is exerted between them. By measuring the voltage balancing the potentials and minimizing the force, which is called contact potential difference (CPD), during scanning over the surface, an image of the electrostatic potential of the sample surface can be taken in a spatial resolution of AFM [18]. Note that only relative values of the surface potential are obtained and imaged in this method. The setup of KFM in NC-AFM consists of a lock-in detection of the force differential signal using the modulation method and a feedback circuit to set the signal at zero [18].

Figs. 2(a)–2(c) are a filled-state STM image, an empty-state STM image, and an AFM image of the Ge(105)-(1×2) surface, respectively. Characteristic features shown in the STM images are similar to those reported previously [13]: bright protrusions are aligned along zigzag lines in the filled-state image while they are aligned almost straight in the empty-state image. According to the theoretical calculation [14], the zigzag lines in the filled-state images are due to the rebonded atoms (yellow, A and B in Fig. 1), and the broad single protrusion in the empty-state image corresponds to the normal dimer (orange, C and D in Fig. 1). The image contrasts of STM are explained by the electronic structure of the surface: the dangling bond states of the normal dimers are located above E_F while those of the rebonded atoms are below E_F. Therefore, significant charge (electron) transfer is expected from the dangling bond states of the normal dimer to those of the rebonded atoms. Because

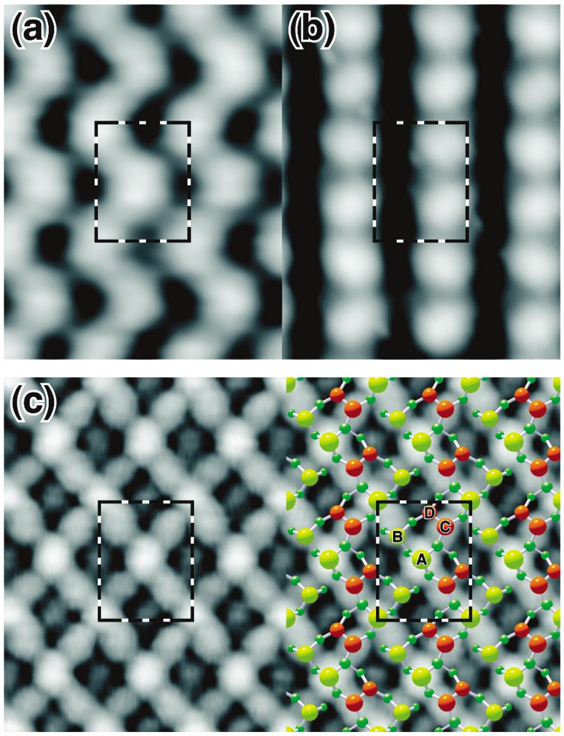

FIG. 2 (color). (a) Filled-state and (b) empty-state STM images taken on the Ge(105)-(1×2) surface formed on the Si(105) substrate. Imaging conditions are -3.0 V and 100 pA for (a), and $+1.5$ V and 50 pA for (b). The rectangular unit cell of the (1×2) structure is depicted in the images. (c) A NC-AFM image taken on the same surface. The frequency shift Δf was set at -60 Hz. The oscillation amplitude A_0 and resonant frequency f_0 of the cantilever were 3.8 nm and 280 482 Hz, respectively. The normalized frequency shift is $\gamma = \Delta f k A_0^{3/2}/f_0 = 2.2\ \mathrm{fN/m^{1/2}}$. The RS model is superimposed on the right half of the image.

of the electronic effect, STM images of neither polarity show all surface atoms having a dangling bond simultaneously.

A corresponding AFM image is quite different from the STM images. In the AFM image [Fig. 2(c)], four types of protrusions, two each, a total of eight in the unit cell, are clearly resolved. Overlapping the RS structural model on the image, these protrusions directly correspond to the positions of the atoms having a dangling bond (A to D in the structure model in Fig. 1). Especially, the atoms composing the normal dimer (C and D) are individually resolved in the AFM image instead of a broad bright spot observed by STM [Fig. 2(b)], demonstrating the higher-spatial resolution of AFM. Furthermore, the height of the protrusions in the AFM image agrees qualitatively with the height of the corresponding atoms calculated without including the tip effect [14]; experimental (theoretical) height differences are about 0.05 nm (0.052 nm) for A with respect to C, 0.0 nm (0.005 nm) for C to B, and 0.04 nm (0.018 nm) for B to D, respectively; D being the most receded.

AFM imaging may be influenced by the force between the tip and surface atoms [19,20]. When the tip is very close to the surface atoms (<0.3 nm), atoms with multicrescents appear in AFM images reflecting the multiple dangling bonds on the tip apex [9,11]. In order to avoid such extra effects we took the highest care by setting the force to a minimum. The force acting on the surface atoms by the tip estimated under the experimental conditions is less than 0.1 nN, small enough to safely neglect the effects of deformation [21] and the multiple dangling bonds [9,11].

Careful inspection of the image, however, reveals that the lateral positions of the receded atom (D) in the AFM image were deviated by 0.2 nm from the one theoretically predicted. We attribute this to the tilted dangling bonds. High-resolution AFM probes the force due to the chemical interaction between the dangling bond of the apex atom on the tip and surface dangling bonds. When dangling bonds extend to the direction tilted from the surface normal, the position of the atom in the AFM image should shift to the tilted direction. The dangling bonds of the dimer composed of atoms C and D point outside on the nanosize (001) terrace, which is tilted from the vicinal surface. One can thus expect that the dangling bond originating from atom D is tilted from the surface normal, causing the deviation in AFM images. Theoretically imaged wave function of the dangling bond states indicates that the dangling bond of atom D protrudes to the direction tilted outside by 20° while the dangling bond of atom C aligns to the perpendicular direction. The tilted dangling bond indeed explains the deviation observed in our AFM images from the core atomic position of the surface. Similar observations were reported in AFM imaging of the dimer structure on the Si(001)-(2×1) surface [22], and qualitatively supported by theoretical AFM simulations [23]. In our experiments we noticed some variation in the lateral positions depending on imaging conditions [i.e., Fig. 2(c) and Fig. 3(a)] [24]. The amount of the deviation is expected to depend on the tip-sample distance during AFM imaging. The force dependence of the positional deviation is now under investigation and will be reported later.

In order to probe the charge transfer directly, we measured a potential profile using the KFM mode. Simultaneously taken topographic (AFM) and potential (KFM) images are shown in Figs. 3(a) and 3(b), respectively. The (1×2) periodicity was clearly observed in both images. Figure 3(c) shows a cross-sectional line

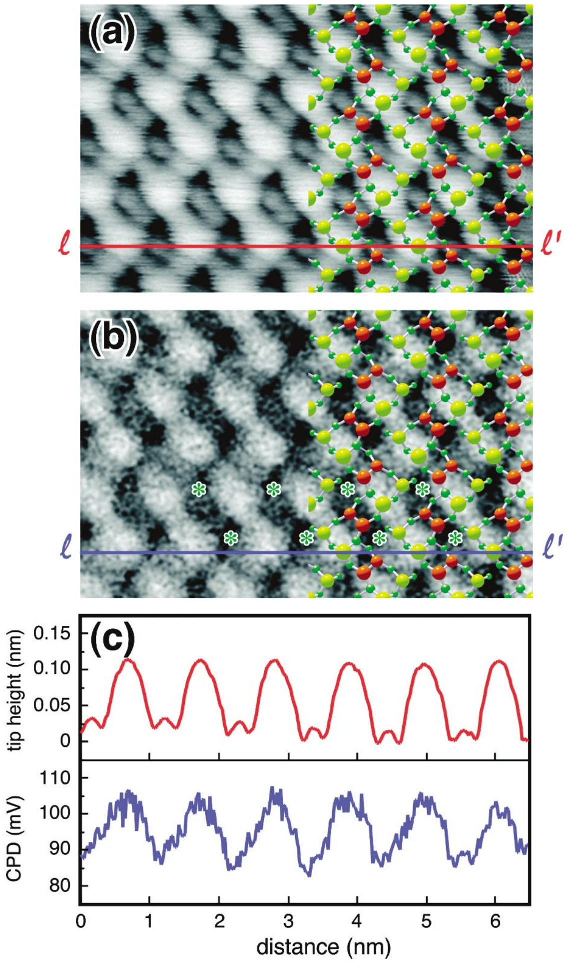

FIG. 3 (color). (a) Topographic NC-AFM and (b) electrostatic potential (KFM) images taken simultaneously on the Ge(105)-(1×2) surface superimposed with the RS model. In the potential image, bright (dark) color indicates high (low) potential, that is, repulsive (attractive) for electrons. The resonance frequency, the spring constant, and the oscillation amplitude of the cantilever were 273 646 Hz, 44 N/m, and 0.9 nm, respectively. The frequency shift was set at −125 Hz for the AFM imaging. For the KFM experiment, a modulated voltage with a frequency of 1.5 kHz and amplitude of 250 $\mathrm{mV_{rms}}$ was applied on the sample bias voltage. (c) Cross-sectional profiles measured on the topographic (a) and potential (b) images along the red and blue $\ell - \ell'$ lines, respectively.

profile taken along the solid line $\ell - \ell'$ in Figs. 3(a) and 3(b). It should be noted that the energy resolution of the surface potential in this method is better than 3 meV, remarkably high compared with any other spatially-averaged work function measurement methods. It is evident from a comparison of the two profiles that the outermost atoms have the highest potential: the potential above A, one of the rebonded atoms, is 15–20 meV higher than D of the normal dimers. When a charge (electron) transfer occurs from one entity to another on the surface, the surface potential becomes lower at the electron-deficient one and higher at the other. Our potential image taken on the Ge surface is, thus, direct evidence of charge transfer from dangling bond states of the normal dimer to those of the rebonded atoms, directly supporting the model predicted from theory and STM images.

The calculated potential profile [21] of the Ge(105)-(1×2) surface of the RS model using a first-principles method shows that the potential on the normal dimers is lower than that on the rebonded atoms, which is qualitatively consistent with our experimental results. Potential differences between the normal dimers and the rebonded atoms rapidly decreases with the normal distance from the surface. According to the theoretical results, the potential difference at the distance of $0.74 \sim 0.80$ nm, which is an estimated distance in our experimental conditions, is about 15–20 meV, consistent with the difference in our measurement. One may notice in the potential image [Fig. 3(b)] that the area where no surface atoms are present, marked with * in the figure, has the lowest potential. The calculated potential profile indicates that the potential above the dipped area is lowered due to the tails of the surrounding atoms' potentials although the atoms in the dip are neutral and have an intermediate potential at the core site. This is consistent with the experimental results.

In conclusion, using the Ge(105)-(1×2) surface we demonstrated high performances of NC-AFM by taking highly resolved AFM images and by taking atomically resolved electrostatic potential images with a KFM method. All surface atoms having a dangling bond state are clearly observed in AFM images, supporting for the model proposed by a collaborative study of STM and first-principles calculation. The atomically resolved potential profile of this surface directly confirms the charge transfer among the dangling bond states. This work demonstrates that atomically resolved NC-AFM is quite useful to determine surface atomic structure without being disturbed by the electronic effect and to obtain surface potential profile with high spatial and energy resolutions.

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