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Description	

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Electric conductance through chemical bonding states being formed between a Si tip and a Si(111)-(7×7) surface by bias-voltage noncontact atomic force spectroscopy

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The change in electric conductance through bonding states being formed between a Si tip and a Si surface is examined by bias-voltage noncontact atomic force spectroscopy: current I and force interaction Δf (AFM cantilever resonance frequency shift) are simultaneously measured versus bias voltage V. A peak in I-V curves appears at close tip-sample separation over adatoms at the same V as a sharp peak in the Δf-V does. The peak possibly corresponds to channel formation through bonding states induced by changing V, leading to current saturation on tunnel barrier collapse with decreasing separation.

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In the last decade the electric current passing in nanostructures has attracted much interest from a viewpoint of basic quantum mechanics as well as intriguing application to nanodevices. One of the representative nanostructures is an atom-size neck between two bodies of condensed matter; the current passing through it is governed mainly by electron channels formed between them.[1] The channels concern the bonding states between atoms constituting the neck. A great number of experimental studies to measure the conductance of nanocontacts and wires between two bodies have aggressively been carried out by breaking them using scanning tunneling microscopy (STM),[2,3] transmission electron microscopy (TEM)-STM combined instruments,[4,5] or mechanically controllable break junctions (MCBs).[6] Understanding of quantized conductance in nanostructures as a quantum effect has progressed, but the relation between conductance and bonding is still questionable. One should precisely evaluate the conductance while forming bonding states by bringing one body closer to the other.

In order to simultaneously measure the current and the force interaction including chemical bonding between two bodies, atomic force microscopy[7] (AFM) is one of the most powerful tools, since the AFM can control a tip-sample separation precisely closer than the STM can by using the force interaction instead of tunneling current. The characteristic curves of force versus tip-sample separation have been measured by the AFM with current I versus distance curves.[8–10] The relation between the force and the current for metals has been studied theoretically:[11,12] the overlapping of wave functions of a tip and a sample is a central issue to elucidate the interaction of chemical bonding and the conductance between two bodies in proximity.

Chemical bonding formation is associated with collapse of a tunneling barrier between two bodies. Tsukada *et al.* calculated the relation between the barrier collapse and current, which changes from tunneling to ballistic, for an Al tip-Si sample system and a Na-Na system with decreasing tip-sample separation by a recursion-transfer matrix method.[13,14] At tip-sample separations below 5 Å the tunneling barrier vanishes so that the current saturates; electrons flow in ballistic through a potential hole at the tip. They showed that electrons distribute over two bodies, leading to chemical bonding.

Noncontact (NC) AFM can depict surfaces with atomic resolution;[15,16] an AFM cantilever is self-oscillated at its resonance frequency, and the frequency shift Δf is measured by frequency modulation technique as a change in the interaction between a sample and a tip at the end of cantilever. We have recently evaluated the force interaction with respect to bias voltage V between them using bias-voltage noncontact atomic force spectroscopy (NCAFS), constructed on basis of NCAFM.[17] Obtained Δf-V curves exhibited prominent peaks, which are attributed to quantum-mechanical resonance induced by changing V. Since the resonance is induced between the electronic states having closer energy levels, the overlapping of wave functions at the energy levels tuned with changing V on the tip and the sample gives an enhanced attractive force between them.

In this paper we report simultaneous measurements of I-V and Δf-V curves by bias-voltage NCAFS for a Si tip and a Si(111)-(7×7) surface. By bringing the tip closer to the sample in a stable manner using the NCAFS, we attain pseudobonding states between them, involving chemical bonding, with tunneling barrier collapse. In comparison of Δf-V with I-V curves, the relation of chemical bonding formation and the conductance are discussed at close separations by changing V.

We used a home-made NCAFM/AFS in 5×10^{-11} Torr with a piezoresistive Si cantilever having a [001]-oriented Si tip with a resonance frequency of 167 kHz and a spring constant of 7 N/m, cleaned by several treatments including heating in ultrahigh vacuum (UHV),[18] and sharpened by a Si-nanopillar epitaxial growth method.[19] The piezoresisitive cantilever has a resistance of 2 kΩ, a change in which due to the cantilever deflection was measured with a Wheatstone bridge under a tip potential of 0.625 V with respect to the ground potential. We refer to the sample potential with respect to the tip potential as the bias voltage V. Since we used no laser optics to detect the cantilever deflection, we conducted the measurements in dark environmental conditions, leading to no optical excitation in the electronic states at semiconductor surfaces. A sample was a cut of an

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n-Si(111):P wafer with a resistivity of 8–12 Ω cm, cleaned by flashing at 1200 °C in UHV, resulting in the 7×7 surface reconstruction.

The current I passing between the tip and the sample was measured using a high-gain current amplifier with a bandwidth of 3 kHz, the input of which was connected to the sample. Since the tip is oscillated at the resonance frequency 167 kHz using a self-oscillation circuit for NCAFM imaging and NCAFS measurement, while keeping amplitude A constant, $A=15.5$ nm, the current periodically increases exponentially with decreasing tip-sample separation. The current amplifier with the bandwidth outputs a time-averaged value of current over one cycle of the cantilever oscillation. Here we assume that the current changes as $I=I_c\exp(-\beta z)$, where $\beta=10.2\sqrt{[\varnothing-(e|V|/2)]}$, z is the tip-sample separation in nm, I_c the extrapolated current at $z=0$, $\varnothing$ the tunneling barrier height, and e the electron charge. By taking the time average of I over one cycle of cantilever oscillation[20,21]

$$\langle I(t)\rangle=\frac{1}{T}\int_0^T I(t)dt=\frac{1}{T}\int_0^T I_c\exp[-\beta(z_0+A)]\times\exp\left(-\beta A\cos\frac{2\pi}{T}t\right)dt, \quad (1)$$

where $z=A[\cos(2\pi/T)t+1]+z_0$, T the period of the cantilever oscillation, and z_0 the closest separation, we obtain the following expression:

$$\langle I(t)\rangle=I(z_0)\exp(-\beta A)\ \text{Bessel}\ I[0,\beta A]. \quad (2)$$

Here, $I(z_0)$ is the current at the closest separation and Bessel $I[\cdots]$ is the modified Bessel function of the first kind. $\langle I\rangle$ is estimated to be a few hundredths of $I(z_0)$ under typical experimental conditions: e.g., 2.2% for $\varnothing=4$ eV, $V=-0.5$ V, $A=15.5$ nm, and $f=1/T=167$ kHz.

For surface observation by the NCAFM, the tip was scanned over a sample surface while maintaining a constant shift of the resonance frequency Δf under a constant amplitude. For the simultaneous measurements by the NCAFS, Δf-V and I-V curves were recorded with changing V in a triangular sawlike wave form with a duration of 100 ms under the constant amplitude, while stopping the tip scan and holding the tip-sample separation instantaneously; an NCAFM image was also obtained simultaneously with the curves recorded at $16\times16=256$ points in a scanning area, similarly to current imaging tunneling spectroscopy (CITS).[22] To examine the separation dependence of Δf-V and I-V curves, we repeated to take the curves at different tip-sample separations. In general, the atomic contrast in NCAFM images diminishes with increasing tip-sample separation. Thus, by retracting the tip by a preset quantity from the sample only when taking the curves under the same imaging conditions, we assigned the measurement position over the sample surface with atomic resolution. We changed the retraction quantity from 0.5 to 0 nm.

Figure 1 shows typical curves over a Si adatom in the faulted half cell of 7×7 and over an area with no Si surface atoms at separations of about 0.9, 0.5, and 0.4 nm, the relative differences of which were precisely evaluated as mentioned above, but the absolute values were not. At 0.9 nm, in Fig. 1(a), the Δf-V curves show parabolic owing to electrostatic force between the tip and the sample, although they slightly deviate at the bottom from the parabolic. This deviation is attributed to the bias dependent force interaction, corresponding to a broad peak in Ref. 17. The contact potential difference was calculated to be −0.42 V from the parabolic curve, not including its bottom part, which was the same in all of the curves. In Fig. 1(a) the current was not detected. With decreasing tip-sample separation to 0.5 nm, a small increase in current was found around −0.45 V over the Si atom in Fig. 1(b), while Δf exhibited an increase at the same voltage. On the other hand, no current increase was found over an area with no Si surface atoms, although a slight increase in Δf as the broad peak was found over the sample surface as reported.[17] Further decreasing up to 0.4 nm, surprisingly we found a prominent current peak around −0.5 V as well as the Δf peak, in Fig. 1(c), though no current increase and no sharp peak in Δf over an area with no Si surface atoms. This indicates that electrons chiefly pass via the bonding states being formed between the tip and the Si atom by tuning the electronic states through changing V, corresponding to the Δf peak, with decreasing tip-sample separation. The peak

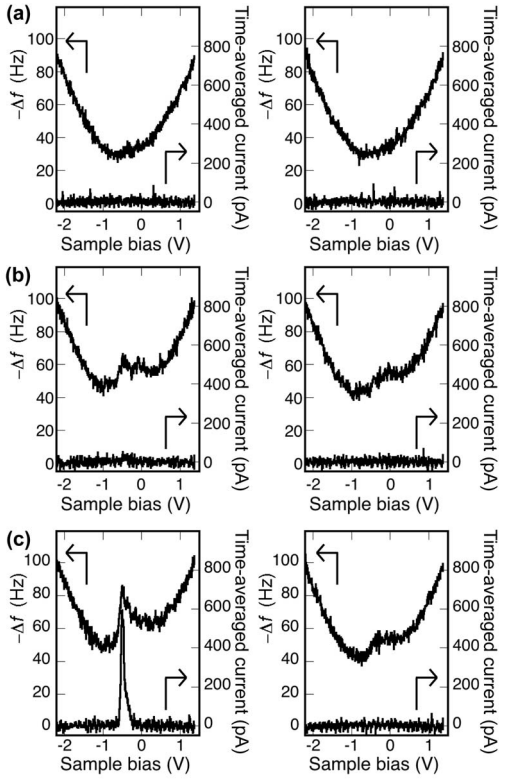

FIG. 1. Δf-V curves (upper) and I-V curves (lower) simultaneously taken by bias voltage NCAFS with the same tip without any change while measurements. The left column shows curves over a corner Si adatom in the faulted half of 7×7, and right column shows curves over an area with no Si surface atoms. (a) At a tip-sample separation of 0.9 nm. (b) At 0.5 nm. (c) At 0.4 nm. The separation values were roughly estimated, but the differences precisely evaluated. A prominent current peak is found together with a maximum Δf peak over the Si atom in (c).

value of the time-averaged current was about 600 pA, which indicates that the maximum current at the closest separation on the cantilever oscillation was estimated to be 20–30 nA as mentioned above, numerically calculated assuming that the current saturates at very close separation from tunneling to ballistic[13] as discussed later. Although the current value seems low as a point contact in ballistic, it is probable that the transmission probability through the Si-Si bonding states being formed is so low, since the tip and the sample are semiconductors and their separation is slightly wider than the Si-Si bonding length in bulk. Note, in addition, that small tunneling current probably passes between the tip and the sample under a bias voltage as high as ~1 V, though we did not detect it, since our measurement system is not so sensitive to detect a low time-averaged current less than 10 pA.

We reported that the Δf-V curves consisted of a number of sharp peaks and a board peak after subtracting the contributions due to electrostatic and van der Waals forces from raw curves.[17] The peaks were enhanced with tuning bias voltage at close separation, and the sharp peaks exhibited atom-site dependence, but the board peak did not. They were attributed to quantum mechanical resonance between the tip states and the sample surface states, corresponding to chemical bonding, and possibly to formation of resonating states over a lowered tunneling barrier, corresponding to metallic bonding, respectively. According to Refs. 11 and 12, the quantum mechanical resonance between the surface electronic states of a tip and a sample through the tunneling barrier is responsible for the force and the tunneling conductance; that is overlapping of their wave functions at close energy levels, although they did not discuss the bias dependence on the force because of metal surfaces with no specific electronic states. In this study both the tip and the sample were semiconductors; a [100]-oriented Si tip probably has an energy gap at the surface having asymmetric Si dimers, and a sample of Si(111)-(7×7) has metallic states at the surface as a half-filled dangling bond of a Si adatom. Since the peak around −0.5 V roughly agrees with that observed by CITS (Ref. 23) for Si adatoms, the overlapping of wave functions between the Si adatom and the buckled down Si atom in the dimer at the tip apex possibly governs force and current between the tip and the sample. Note that, depending on the atomic sites on the surface, the peak voltage of current slightly shifted together with that of the maximum Δf peak. The current peak has a tail on the right side, possibly because of weak overlapping between other states of the tip and the sample, which leads to smaller Δf peaks on the right side of the maximum peak in Fig. 1(c). In addition, note that current detection around 0 V is not easy, since it decreases linearly with V.

In order to elucidate the increase of I and Δf at the peak bias voltage with decreasing separation, we took the I- and Δf-distance curves at $V=-0.5$ and −0.2 V. Figure 2 shows the curves with current images simultaneously obtained on the measurements, where a z-feedback was controlled by the NCAFM at a low feedback gain; since the tip-sample separation was roughly constant, the current images exhibited atomic contrast but the NCAFM imaged did not. While stopping the scan and holding the z-feedback control, we retracted the tip at 256 points in the image. In Fig. 2, red

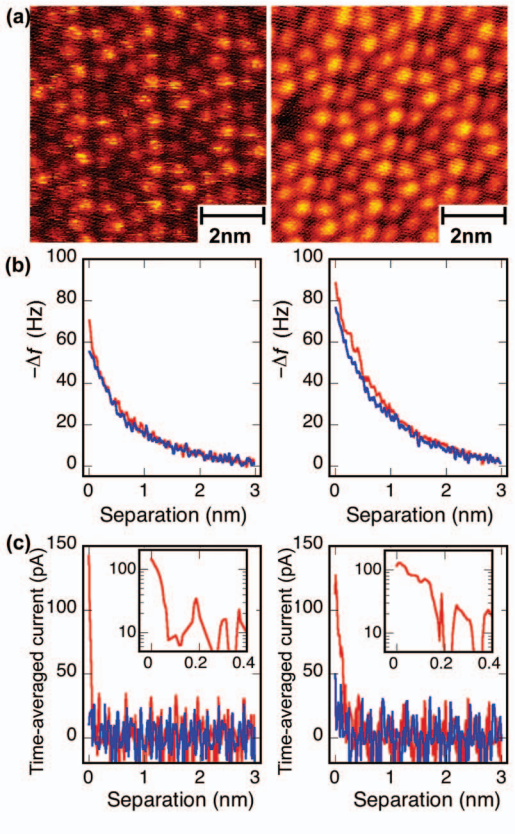

FIG. 2. (Color) Δf and time-averaged current I versus tip-sample separation at $V=-0.5$ and −0.2 V, in left column and right column, respectively. Red curves over a corner Si adatom and blue curves over an area with no Si surface atoms. (a) Current I images simultaneously obtained at $\Delta f=58$ and 82 Hz for −0.5 and −0.2 V, respectively. (b) Δf-distance curves. (c) I-distance curves simultaneously obtained with (b). Insets show log-scaled I around close separation.

curves were taken over a corner Si adatom in the faulted half cell of 7×7 and blue over an area with no Si surface atoms. By comparing tip displacements under these imaging conditions, the closest tip-sample separation in Fig. 2 at −0.2 V was found roughly 0.15–0.2 nm closer than that at −0.5 V. In Fig. 2(b), the red curves exceed blue curves at close separation for both bias voltages; the difference of Δf between red and blue curves should correspond to net chemical bonding between the corner Si adatom and the Si tip. Note that Δf over the adatom at −0.5 V increased abruptly at very close separation compared with that at −0.2 V. This indicates that the surface states were tuned more tightly at −0.5 V than −0.2 V, in agreement with the characteristics of Δf-V curves.

The I-distance curves simultaneously obtained show a rapid increase over the adatom with decreasing tip-sample separation, in Fig. 2(c). An increase over the area with no Si surface atoms was found at the closer separation at −0.2 V, since the origin of the abscissa is 0.15–0.2 nm closer to the sample than that at −0.5 V. Insets in Fig. 2(c) show the change of I over the adatom on a logarithmic scale around very close separation. As the tip is closer to the sample, the increase in current saturates on the scale. From the slopes of

ln I around the closest separations at −0.2 and −0.5 V, by taking account of the current measurement time averaged over the cantilever oscillation, we estimated the apparent barrier heights to be less than 1 and 2 eV, respectively. These values are less than a barrier height of ~4 eV at wider separations for Si. Accordingly to Ref. 13, the net barrier height is close to zero around a tip-sample separation of 0.5 nm, although the current still remains increasing with decreasing separation. By taking the derivative of a ln I-separation curve in Fig. 2 in Ref. 13, we calculated the apparent barrier height around a separation less than 0.5 nm to be 1–2 eV. Tsukada *et al.* pointed out that the current saturation with decreasing tip-sample separation indicates the tunneling barrier collapse or formation of a hole in the barrier around the tip apex, leading to chemical bonding owing to electron spreading over two electrodes.[13] The abrupt increase in current at −0.5 V is possibly attributed to the tunneling barrier collapse enhanced by electron redistribution over the tip and the sample due to the resonance states tuned with the bias voltage.

In addition, it is noted that the relaxation of the tip atom and the sample atom in proximity should be taken into account to explain the bias dependence, which can enhance the current increase and saturation owing to the attractive force between them, leading to a narrow separation between the tip and the sample. According to the calculation of Pérez *et al.*,[24] where the bias voltage is not applied, a Si atom at a [111]-oriented Si tip apex, and a Si adatom on a faulted half cell of Si(111)-(5×5) are perceptibly relaxed at a separation of less than 5 Å; as a result, the separation becomes 0.5 Å narrower at the maximum than that for case with no atomic relaxation, and the relaxation disappears at 2.35 Å, where the atoms are located at their equilibrium positions. In our experiments, the atomic relaxation can be induced under strong attractive interaction due to a close separation. Thus, the peaks in I- and Δf-V curves is possibly enhanced, since the true separation may become closer, about 0.5 Å at maximum, than that estimated from the z piezo displacement, while the displacement was held constant by inactivating the z-feedback control. Although this separation narrowing can accelerate the opening of conductance channel under strong chemical interaction with the bias dependence, the obtained I- and Δf-V curves clearly show that the conductance channel formation is deeply correlated with the chemical bond formation.

In conclusion, by bringing a tip closer to a sample, we have measured the change in electric conductance through bonding states being formed between a Si tip and a Si(111)-(7×7) surface by bias-voltage noncontact atomic force spectroscopy with changing bias voltage V; current I and the resonance frequency shift Δf versus V were simultaneously recorded. A peak in I-V curves prominently appeared at close tip-sample separation over Si adatoms at the same V as a sharp peak in Δf-V did. The peak possibly corresponds to conductance channel formation through bonding states induced by changing V, where the current saturates from tunneling to ballistic on tunneling barrier collapse with decreasing separation. This also evidenced that the overlapping of wave functions of a tip and a sample can be tuned through changing V, leading to enhanced force interaction. The bias voltage NCAFM/AFS can be a powerful tool for analysis and control of the conductance and the bonding states between nano structures in proximity, including molecular nano devices with covalent bonding states, the nature of which drastically changes with separation and bias voltage.

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