LETTERS

Local and Reversible Change of the Reconstruction on Ge(001) Surface between $c(4\times2)$ and $p(2\times2)$ by Scanning Tunneling Microscopy

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The reconstruction on a Ge(001) surface is locally and reversibly changed between $c(4\times2)$ and $p(2\times2)$ by controlling the bias voltage of a scanning tunneling microscope (STM) at 80 K. It is $c(4\times2)$ with the sample bias voltage $V_b \leq -0.7$ V. This structure can be maintained with $V_b \leq 0.6$ V. When V_b is higher than 0.8 V during the scanning, the structure changes to $p(2\times2)$. This structure is then maintained with $V_b \geq -0.6$ V. The observed local change of the reconstruction with hysteresis is attributed to the energy transfer process from the tunneling electron to the Ge lattice in the electric field under the STM tip.

Local modification of surface structure on the atomic scale has been demonstrated using scanning tunneling microscopes (STMs). Surface adatoms were reversibly manipulated first on a Ni surface at low temperature.[1] On the other hand on semiconductor surfaces, the modifications by temporal voltage pulses, such as the removals of surface atoms[2–4] and adsorbed hydrogen,[5,6] have been performed. Up to now, however, there has been no report on the reversible modification of local surface reconstructions using STM.

Such modification can be expected on the ground state $c(4\times2)$ reconstructed surface of Ge(001) as well as Si(001) because the energy difference between the ground state and the $p(2\times2)$ structure is estimated to be a few meV/dimer.[7–9] On both surfaces, the two neighboring atoms form a buckled dimer, and their reconstructions are characterized by the ordering of the buckled dimers.[10] Experimentally, fluctuation between the $c(4\times2)$ and $p(2\times2)$ structures was induced from defects on Si(001)[11] or from Ag adsorbates on Ge(001)[12] surfaces. Recently, the reconstructed structure of a clean Si(001) surface was studied in detail at low temperatures by STM.[13] One of the three structures, 2×1, $p(2\times2)$ and $c(4\times2)$ is observed, depending on both the sample bias voltage and the dopant species. This suggests that the band bending at the subsurface plays an important role in fixing the structure as well as the electric field between the STM tip and the surface. It has been argued that the ground state energy of the Si(001) surface is partly determined by the electrostatic energy among the electric dipole moments at the dimers.[14] In contrast to the extensive studies on Si(001), the ground state of Ge(001) has not yet been thoroughly investigated, while the $c(4\times2)$ reconstruction was generally observed below 150 K.[15,16] To date, the transition induced by the bias voltage change of STM has been reported only from $c(4\times2)$ to $p(2\times2)$ on a vicinal Ge(001) surface.[17]

In the present letter, we show reversible change between $c(4\times2)$ and $p(2\times2)$ structures on a clean Ge(001) surface, which can be locally controlled by the sample bias voltage V_b of STM with hysteresis below 80 K. The $c(4\times2)$ structure is observed at negative $V_b \leq -0.7$ V while the $p(2\times2)$ is

observed at positive $V_b \geq 0.8$ V. Both structures can be maintained even while scanning the surface with $|V_b| \leq 0.6$ V at 80 K. These findings are important for the fundamental understanding of the stability of the reconstructed surface.

All experiments were performed in an ultrahigh-vacuum (UHV) system with a base pressure of below 1×10^{-8} Pa consisting of a commercial variable-temperature scanning tunneling microscope (OMICRON, LT-STM) and a surface preparation chamber.[12] Germanium specimens were cut to the size of $8 \times 3 \times 0.4$ mm^3 from a Ge(001) wafer (Sb-dope, 0.35 Ω·cm at room temperature). The Ge(001) clean surfaces were obtained by several repetitions of Ar ion bombardment (1 keV, 2.5 μA·cm^{-2}, 10 min) and annealing at 980–1000 K for 10 min by passing DC current directly through the specimen in the UHV preparation chamber. Then, the specimen was transferred to the STM, and the surface was observed at 80 K or 10 K with a tungsten tip in a constant current mode.

Figure 1 shows a series of STM images obtained successively with three values of V_b on the same area of Ge(001) surface at 80 K. In the case of $V_b = -2.0$ V the surface superstructure is $c(4\times2)$ as shown in Fig. 1(a). We can maintain this structure when V_b is less than 0.6 V. Figure 1(b) shows the image with $V_b = -0.2$ V. When we further increase the bias to 1.2 V, the structure becomes $p(2\times2)$ as shown in Fig. 1(c). Then, this structure can be maintained with V_b down to -0.6 V across the zero bias as demonstrated in Fig. 1(d) for $V_b = -0.2$ V. The bias dependence of the surface reconstruction at 80 K is summarized in Fig. 1(e). We can fix either of the two structures at the same bias by changing the bias from $V_b \geq 0.8$ V or $V_b \leq -0.7$ V to $|V_b| \leq 0.6$ V. It is noted that both structures can be maintained without an electric field due to the STM tip; even after keeping the tip apex 500 nm away from the area of interest for 5 min, we observed again the same local structure at the area. The surface structure at 10 K depends on V_b in the same way as that at 80 K. The observed bistability at $|V_b| \leq 0.6$ V indicates an energy barrier between the $c(4\times2)$ and $p(2\times2)$ structures. At the structural change, a flip process of the buckled dimers occurs in the $c(4\times2)$ or $p(2\times2)$ domain. The energy required for such a process in the $c(4\times2)$ domain was theoretically estimated to be 416.7 meV based on a first-principles calculation.[18]

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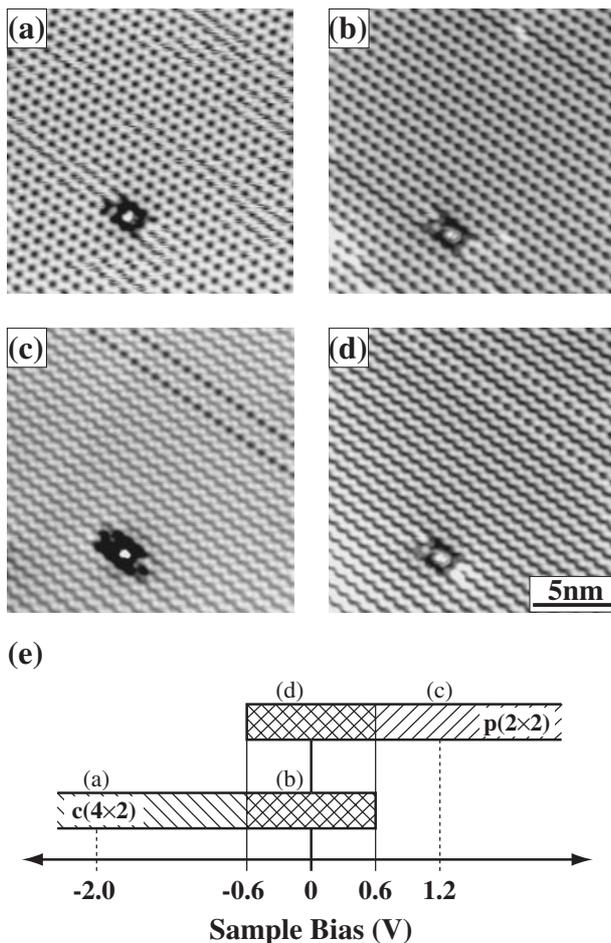†E-mail: komori@issp.u-tokyo.ac.jp

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Fig. 1. (a–d) STM images of the same area ($18 \times 18\,\mathrm{nm}^2$) on a clean Ge surface at 80 K with different sample bias voltages; (a) $-2.0\,\mathrm{V}$, (b) $-0.2\,\mathrm{V}$ changed from a negative bias, (c) $1.2\,\mathrm{V}$, (d) $-0.2\,\mathrm{V}$ changed from a positive bias. Tunneling current was 0.43 nA. (e) A schematic showing the observed superstructures depending on the sample bias voltage and the direction of the voltage change.

Fig. 2. (a–c) STM images of the same area ($20 \times 20\,\mathrm{nm}^2$) of a clean Ge(001) surface. They are selected from the successive images (7 min interval) after the V_b change from $-2.5\,\mathrm{V}$ to $1.2\,\mathrm{V}$ at 80 K; (a) 1st image (b) 3rd image (c) 7th image. Tunneling current was 0.2 nA. Arrows in the figures indicate the sudden change of the buckling phase of the Ge dimer. (d) A tunneling spectrum of a clean Ge(001) surface at 10 K.

When we increase V_b for several ms from $-2.5\,\mathrm{V}$ to $+1.2\,\mathrm{V}$ and continue to scan the surface, the surface gradually transforms from $c(4 \times 2)$ to $p(2 \times 2)$ through a random series of sudden flips of the dimers at a single Ge dimer row as in Figs. 2(a)–2(c). Here, we show selected successive STM images after the V_b change. Arrows in the figures indicate the sudden changes of the dimer phase during the scanning of the surface from the bottom of the image to the top. When the buckling direction of a dimer changes, all dimers in the same dimer row change simultaneously. That is, the change of the dimer phase continues to the outside of the scanning area along the dimer row until the dimer row is terminated by steps or defects. The transformation of the structure was also observed from $p(2 \times 2)$ to $c(4 \times 2)$ when we decrease V_b, for example, from $+2.0\,\mathrm{V}$ to $-1.2\,\mathrm{V}$. In contrast to the change from $c(4 \times 2)$ to $p(2 \times 2)$, however, this change is limited to a few nm away from the area of the scanning along the dimer-row direction. At the boundaries between the $c(4 \times 2)$ and $p(2 \times 2)$ areas, there form pairs of the adjacent dimers along the dimer-row direction with the same buckling direction.

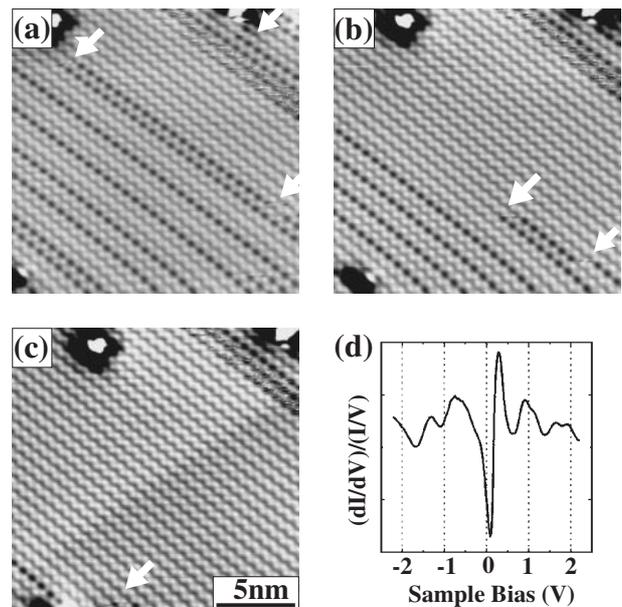Figure 2(d) shows a scanning tunneling spectrum spatially averaged on a clean Ge(001) surface at 10 K. The observed peaks at $-1.25\,\mathrm{V}$ and $+1.05\,\mathrm{V}$ are consistent with the previous result obtained at RT.[16] All the peaks appearing between -1.0 and $1.0\,\mathrm{V}$ are attributed to the dangling bond π and π^* states as in the Si(001) surface.[19] The positions of the peaks in the tunneling spectra move toward $V_b = 0$ at 80 K. This is mainly ascribed to the temperature dependence of the band bending near the surface.

The $c(4 \times 2)$ and $p(2 \times 2)$ structures are characterized by the phase difference between two adjacent dimer rows. If the dimers are all in phase, the domain structure is $p(2 \times 2)$, and if they are out of phase, it is $c(4 \times 2)$. Here we define the "$c(4 \times 2)$ length" of an area as the total length of the phase-mismatched adjacent dimers along the dimer-row direction. We estimated the change rate from $c(4 \times 2)$ to $p(2 \times 2)$ by measuring the $c(4 \times 2)$ length in successive images of the same area as a function of time after a sudden V_b increase, at several values of the tunneling current, I_t. The results are shown in Fig. 3 for the V_b change from $-2.0\,\mathrm{V}$ to $0.8\,\mathrm{V}$. It took 6 min to obtain each image of $50 \times 50\,\mathrm{nm}^2$. The $c(4 \times 2)$ length after the first scanning decreases with increasing I_t. The buckling phases of a few dimer rows on this surface could not be changed by the scanning with $V_b = 0.8\,\mathrm{V}$ because the phase is firmly fixed by defects on the surface. Apart from these dimer rows, the characteristic times for the structural change are less than 6 min for $I_t = 1.6\,\mathrm{nA}$ and 12 min for 0.8 nA.

We confirmed that the tip moves toward the surface by just 0.06 nm with increasing tunneling current from 0.4 nA to 2 nA at $V_b = 1.2\,\mathrm{V}$. This value is less than 10% of the tip–surface distance under the typical tunneling condition. While the tunneling current increases by a factor of 5, the electric field and the attractive atomic force between the tip and the surface change within 10%. Thus, the transition of the buckling phase is not attributed directly to the electric field or
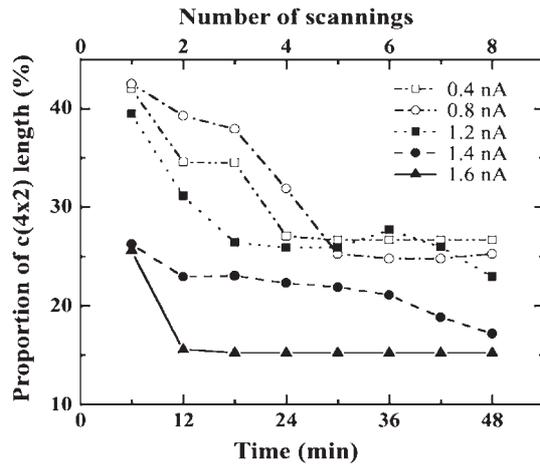
Fig. 3. Proportion of the total length of the phase-mismatched two adjacent dimers indicating the $c(4\times2)$ superstructure [$c(4\times2)$ length] in successive eight STM images of the same area after a sudden V_b change from -2.0 V to 0.8 V at five values of tunneling current between 0.4 nA and 1.6 nA. The STM images were taken at a 6 min interval. During the first scanning, the length decreased rapidly with increasing I_t.

to the atomic force, but to an energy transfer process from the tunneling electron to the Ge lattice.

The phase of the dimer row suddenly changes during the scanning as shown in Fig. 2. The initial change rate, R_t, obtained from Fig. 3 is of the order of 10^{-11}/dimer-row/electron at $V_b = 0.8$ V. It increases with increasing V_b. For example, R_t at $V_b = 1.2$ V is more than one order of magnitude larger than that at $V_b = 0.8$ V. On the other hand, we can maintain both superstructures for more than 2 h during the scanning on the surface with $V_b = \pm0.6$ V and $I_t = 1$ nA at 80 K. The change rate with $V_b = 0.8$ V and $I_t = 1$ nA decreases to about 1/3 upon decreasing temperature from 80 K to 10 K. According to the tunneling spectrum shown in Fig. 2(d), electrons are effectively injected into or removed from the dangling bond π or π^* states by tunneling when $|V_b| \geq 0.7$ V.

Another mechanism for flipping dimers was proposed for the Si(001) surface.[20] It was theoretically demonstrated that the strong tip–dimer interaction induces a flip–flop motion of the dimer. This would explain the 2×1 structure observed by STM below 40 K on a clean Si(001) surface.[13] On this surface, the configuration of the dimers was observed symmetrically with increasing the tip–surface interaction, that is, with decreasing $|V_b|$ or increasing I_t. On the Ge(001) surface, however, the observed flipping of the dimers is inconsistent with the tip–dimer interaction model. The flipping rate of the Ge dimer rapidly decreased with decreasing V_b from 1.2 V to 0.4 V at $I_t = 1$ nA. We confirmed that this bias-change decreased the tip–surface distance by 0.34 nm. At the present tunneling condition ($|V_b| \geq 0.4$ V and $I_t \leq 2$ nA), the tip–dimer interaction is not sufficiently strong to flip the Ge dimer. The difference compared to the Si(001) surface is ascribed to the large energy barrier between the $c(4\times2)$ and $p(2\times2)$ structures in Ge(001).[8,9] Experimentally it is plausible that the tip–surface distance on the Si(001) surface is shorter than that on the Ge(001) surface. Unfortunately, the distance has not yet been measured on the Si(001)-2×1 surface below 40 K.

Figures 4(a)–4(d) demonstrate the successive formations
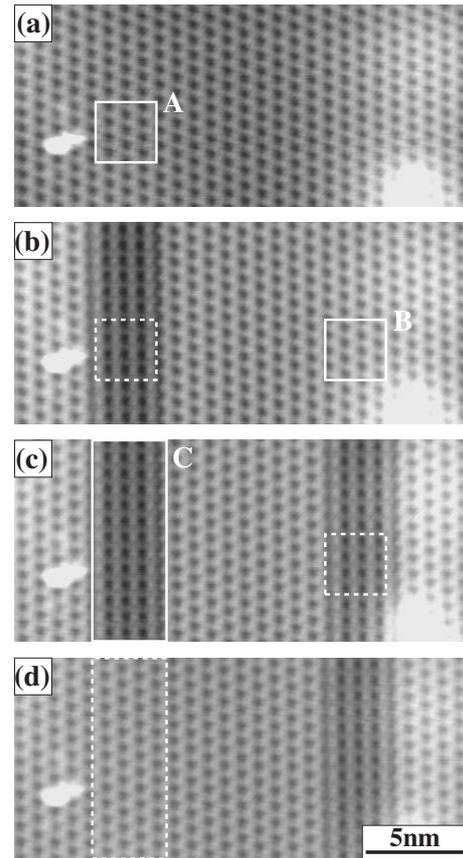

Fig. 4. STM images of the same area (22.5×10 nm^2) of a clean Ge(001) surface at 80 K, with $V_b = -0.2$ V and $I_t = 0.4$ nA. The square areas "A" in (a) and "B" in (b) were scanned with $V_b = 0.8$ V to change the local structure from $c(4\times2)$ to $p(2\times2)$ after taking each image. The surface after scanning "A" is shown in (b), and that after scanning "B" is in (c). The rectangular area "C" in (c) was scanned with $V_b = -0.7$ V to change it from $p(2\times2)$ to $c(4\times2)$. The surface after scanning the area "C" is shown in (d).

and annihilations of local $p(2\times2)$ areas by scanning the small area shown as white rectangles at 80 K. The images were observed with $V_b = -0.2$ V. After taking the image shown in Fig. 4(a), the area A in the figure was scanned with $V_b = 0.8$ V to change from $c(4\times2)$ to $p(2\times2)$. We reduced V_b as low as possible to avoid any influence on the dimer rows outside of the scanning area. The result is shown in Fig. 4(b). The change along the dimer row continued to the outside of the scanning area as described above. Then we scanned area B in Fig. 4(b) to form another $p(2\times2)$ area. The result is shown in Fig. 4(c). The reverse change from $p(2\times2)$ to $c(4\times2)$ was achieved by scanning area C in Fig. 4(c) with $V_b = -0.7$ V. In this case, we had to scan all of the desired $p(2\times2)$ area because the change to $c(4\times2)$ was limited to near the area of the scanning. The annihilation of $p(2\times2)$ is shown in Fig. 4(d). Various nanopatterns can be formed by using local and temporal changes of the bias voltage.

The ground state of the Ge(001) surface has been believed to be the $c(4\times2)$ structure. Both LEED observation[15] and STM study[16] reported the $c(4\times2)$ structure at low temperature, which is consistent with the theoretical studies.[7–9] The surface superstructure of Ge(001) is determined by minimizing two competing energies. One is the strain energy at the subsurface lattice,[9] and the other is the mutual electric-dipole

energy among the Ge dimers.[14] On this surface, the second-layer atoms under the upper atom of the dimer are pulled closer while those under the lower atom are pushed apart to minimize the lattice distortion energy due to the asymmetric dimer. In the $c(4\times2)$ structure, the upper atom of a dimer is adjacent to the upper atom in its adjoining dimer row while it is adjacent to the lower atom in the $p(2\times2)$ structure. Thus, the strain energy of the $c(4\times2)$ structure at the subsurface is lower than that of the $p(2\times2)$ structure. On the other hand, the dipole interaction energy in the $p(2\times2)$ structure is smaller than that in the $c(4\times2)$ because the dipoles are oriented to the same direction in $p(2\times2)$. We note that the upper atom of the dimer is negatively charged and the lower positively. The $c(4\times2)$ structure can be the ground state because the energy gain of the lattice strain dominates the loss of the dipolar energy in this structure. The difference in energy between $p(2\times2)$ and $c(4\times2)$ is as small as 3 meV/dimer.[9]

When the surface is positively biased under the STM tip, the negatively charged upper atoms of the dimers are electrostatically pushed toward the subsurface by the tip, and the lower atoms of the dimers are pulled toward the surface. This makes the difference of the subsurface strain energy between the $p(2\times2)$ and $c(4\times2)$ structures smaller than that without any electric field. On the other hand, the dipole energy in the $p(2\times2)$ structure is still smaller than that in the $c(4\times2)$ structure. Thus, for the positively biased surface, the $p(2\times2)$ structure can be the ground state. In the case of the negative V_b, the buckling of the dimers is increased by the electric field, and the $c(4\times2)$ structure is more stabilized. This mechanism is qualitatively consistent with the stable structures observed at positive and negative biases by STM.

At present, however, we can quantitatively infer neither the variation of the stability difference between the $c(4\times2)$ and $p(2\times2)$ structures nor the flipping probability of a dimer by inelastic electron tunneling under the electric field due to the tip-sample bias. The first-principles calculation of these parameters seems very difficult because the rather long-scale band bending of the Ge subsurface possibly requires extremely large-scale calculations, for example. To clarify the transition mechanism in detail, we should address the above two parameters, which are largely dependent on the local electric field and the local current at the dimer.

In conclusion, we have demonstrated the local modification of the Ge(001) reconstruction between $c(4\times2)$ and $p(2\times2)$ reversibly by V_b change using STM below 80 K. The two different structures coexist with $|V_b| \leq 0.6$ V. The $p(2\times2)$ structure can be the ground state under an electric field, and the local transformation of the structure is attributed to the energy transfer process from the tunneling electron to the lattice.

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