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

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The reconstruction on a Ge(001) surface is locally and reversibly changed between \( c(4 \times 2) \) and \( p(2 \times 2) \) by controlling the bias voltage of a scanning tunneling microscope (STM) at 80 K. It is \( c(4 \times 2) \) 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 \( p(2 \times 2) \). 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.

KEYWORDS: Ge(001) surface, scanning tunneling microscope, inelastic tunneling process, reconstruction, \( c(4 \times 2) \), \( p(2 \times 2) \)

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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. On the other hand on semiconductor surfaces, the modifications by temporal voltage pulses, such as the removals of surface atoms and adsorbed hydrogen, 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 \( c(4 \times 2) \) reconstructed surface of Ge(001) as well as Si(001) because the energy difference between the ground state and the \( p(2 \times 2) \) structure is estimated to be a few meV/dimer. On both surfaces, the two neighboring atoms form a buckled dimer, and their reconstructions are characterized by the ordering of the buckled dimers. Experimentally, fluctuation between the \( c(4 \times 2) \) and \( p(2 \times 2) \) structures was induced from defects on Si(001) or from Ag adsorbates on Ge(001) surfaces. Recently, the reconstructed structure of a clean Si(001) surface was studied in detail at low temperatures by STM. One of the three structures, \( 2 \times 1 \), \( p(2 \times 2) \) and \( c(4 \times 2) \) 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. In contrast to the extensive studies on Si(001), the ground state of Ge(001) has not yet been thoroughly investigated, while the \( c(4 \times 2) \) reconstruction was generally observed below 150 K. To date, the transition induced by the bias voltage change of STM has been reported only from \( c(4 \times 2) \) to \( p(2 \times 2) \) on a vicinal Ge(001) surface.

In the present letter, we show reversible change between \( c(4 \times 2) \) and \( p(2 \times 2) \) 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 \( c(4 \times 2) \) structure is observed at negative \( V_b \leq -0.7 \) V while the \( p(2 \times 2) \) 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 \( 1 \times 10^{-8} \) Pa consisting of a commercial variable-temperature scanning tunneling microscope (OMICRON, LT-STM) and a surface preparation chamber. Germanium specimens were cut to the size of \( 8 \times 3 \times 0.4 \) mm 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 \( c(4 \times 2) \) 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 \( p(2 \times 2) \) 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 \( c(4 \times 2) \) and \( p(2 \times 2) \) structures. At the structural change, a flip process of the buckled dimers occurs in the \( c(4 \times 2) \) or \( p(2 \times 2) \) domain. The energy required for such a process in the \( c(4 \times 2) \) domain was theoretically estimated to be 416.7 meV based on a first-principles calculation.

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When we increase $V_b$ for several ms from $-2.5$ V to $+1.2$ V and continue to scan the surface, the surface gradually transforms from $c(4\times2)$ to $p(2\times2)$ 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 $p(2\times2)$ to $c(4\times2)$ when we decrease $V_b$, for example, from $+2.0$ V to $-1.2$ V. In contrast to the change from $c(4\times2)$ to $p(2\times2)$, 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 $c(4\times2)$ and $p(2\times2)$ 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 $-1.25$ V and $+1.05$ V are consistent with the previous result obtained at RT. The all peaks appearing between $-1.0$ and $1.0$ V are attributed to the dangling bond $\pi^*$ states as in the Si(001) surface. The positions of the peaks in the tunneling spectra move toward $V_b$ change from $-2.5$ V to $1.2$ V at 80 K. This is mainly ascribed to the temperature dependence of the band bending near the surface.

The $c(4\times2)$ and $p(2\times2)$ structures are characterized by the phase difference between two adjacent dimer rows. If the dimers are all in phase, the domain structure is $p(2\times2)$, and if they are out of phase, it is $c(4\times2)$. Here we define the “$c(4\times2)$ 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 $c(4\times2)$ to $p(2\times2)$ by measuring the $c(4\times2)$ 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 $-2.0$ V to $0.8$ V. It took 6 min to obtain each image of $50 \times 50$ nm$^2$. The $c(4\times2)$ 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 $V_b = 0.8$ 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 $I_t = 1.6$ 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 $V_b = 1.2$ 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...
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, \( R_i \), obtained from Fig. 3 is of the order of \( 10^{-11}/\text{dimer-row/electron} \) at \( V_b = 0.8 \text{ V} \). It increases with increasing \( V_b \). For example, \( R_i \) at \( V_b = 1.2 \text{ V} \) is more than one order of magnitude larger than that at \( V_b = 0.8 \text{ V} \). On the other hand, we can maintain both superstructures for more than 2h during the scanning on the surface with \( V_b = \pm 0.6 \text{ V} \) and \( I_t = 1 \text{ nA} \) at 80 K. The change rate with \( V_b = 0.8 \text{ V} \) and \( I_t = 1 \text{ nA} \) 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 \( \pi \) or \( \pi^* \) states by tunneling when \( |V_b| \geq 0.7 \text{ V} \).

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\( \times \)2 structures in Ge(001).\(^8,9\) Experimentally, it is plausible that the tip–surface interaction 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 \( I_t = 1 \text{ nA} \). We confirmed that this bias-change decreased the tip–surface distance by 0.34 nm. At the present tunneling condition (\( |V_b| \geq 0.4 \text{ V} \) and \( I_t \leq 2 \text{ nA} \)), 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).\(^{5,9}\) 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\( \times \)1 surface below 40 K.

Figures 4(a)–4(d) demonstrate the successive formations 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 \( V_b = -0.2 \text{ V} \) and \( I_t = 0.4 \text{ nA} \). After taking the image shown in Fig. 4(a), the area A in the figure was scanned with \( V_b = 0.8 \text{ V} \) 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 \( V_b = -0.7 \text{ V} \) to change it from \( p(2\times2) \) to \( c(4\times2) \). The surface after scanning the area “C” is shown in (d).
energy among the Ge dimers. 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 \(c(4 \times 2)\) 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 \(p(2 \times 2)\) structure. Thus, the strain energy of the \(c(4 \times 2)\) structure at the subsurface is lower than that of the \(p(2 \times 2)\) structure. On the other hand, the dipole interaction energy in the \(p(2 \times 2)\) structure is smaller than that in the \(c(4 \times 2)\) because the dipoles are oriented to the same direction in \(p(2 \times 2)\). We note that the upper atom of the dimer is negatively charged and the lower positively. The \(c(4 \times 2)\) 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 \(p(2 \times 2)\) and \(c(4 \times 2)\) is as small as 3 meV/dimer. 

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 \(p(2 \times 2)\) and \(c(4 \times 2)\) structures smaller than that without any electric field. On the other hand, the dipole energy in the \(p(2 \times 2)\) structure is still smaller than that in the \(c(4 \times 2)\) structure. Thus, for the positively biased surface, the \(p(2 \times 2)\) 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 \(c(4 \times 2)\) 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 \(c(4 \times 2)\) and \(p(2 \times 2)\) 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 \(c(4 \times 2)\) and \(p(2 \times 2)\) reversibly by \(V_b\) change using STM below 80 K. The two different structures coexist with \(|V_b| \leq 0.6\) V. The \(p(2 \times 2)\) 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.