

Rewritable nanopattern on a Ge(001) surface utilizing $p(2\times 2)$ -to- $c(4\times 2)$ transition of surface reconstruction induced by a scanning tunneling microscope

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We present rewritable, nanometer-scale patterns formed on Ge(001) at 80 K, which are based on the transition between $c(4\times 2)$ and $p(2\times 2)$ surface reconstructions induced by a scanning tunneling microscope (STM). We have found that a negative (-0.8 V and 0.5 s) sample bias voltage pulse creates a $c(4\times 2)$ -reconstructed domain of $\sim 1.6\times 2.0$ nm² in a $p(2\times 2)$ -reconstructed region. Applying the negative pulses at appropriate positions, we form an intended pattern of the $c(4\times 2)$ reconstruction. The course of patterning can be monitored by STM with a small bias voltage (-0.2 V) without affecting the written pattern. The whole region can be initialized to the $p(2\times 2)$ by a scan with the bias voltage of $+0.8$ V. © 2004 American Institute of Physics. [DOI: 10.1063/1.1668324]

It has long been investigated to apply scanning tunneling microscopy (STM) to patterning or fabrication of surfaces in nanometer scale. Two approaches have mainly been pursued: one is manipulation of individual atoms or molecules, and the other is surface modification through tunneling-current induced chemical reactions. Well-known examples of the former are Xe atoms on Ni(110)¹ and Fe atoms on Cu(111)² manipulated at 4.2 K. A typical example of the latter is hydrogen desorption from a H-passivated Si(001) surface with the STM tip.³ However, these patterning processes suffer from the fact that it is carried out at a very low temperature or that the patterning is allowed only once. In this letter, we report nanopatterning based on a reversible, *physical* change induced by a STM. It makes the nanopatterning to be rewritable and very simple.

We utilize two nearly degenerate reconstructions of a clean Ge(001) surface. Similar to the case of Si(001), top-most Ge atoms on the (001) surface form asymmetric dimers where one atom in the dimer goes up and the other goes down. The dimers form so-called dimer rows extending along $\langle 110 \rangle$ directions, and the dimers are buckled alternately in a dimer row. Although thermally activated rapid flip–flip of the asymmetric dimer gives rise to a STM image composed of apparently symmetric dimers at room temperature, the image changes to that composed of asymmetric dimers at 80 K.⁴ As illustrated in Fig. 1, there are two possibilities in the relative phase between neighboring dimer rows. The surface reconstruction is recognized to be $c(4\times 2)$ when the buckling in neighboring dimer rows is out-of-phase and it is $p(2\times 2)$ when the buckling is in-phase. These reconstructions are converted to each other by flipping the buckled dimers in every other row. The dominance of the $c(4\times 2)$ reconstruction over the $p(2\times 2)$ has been established by various surface science techniques.^{5–7} A recent theoretical calculation also showed that the $c(4\times 2)$ reconstruction is

stabler than the $p(2\times 2)$, but that the energy difference is very small (1.2 meV/dimer).⁸

Recently, we found that the surface changes from $c(4\times 2)$ to $p(2\times 2)$ during STM observation at positive sample bias voltage (V_b), and that the surface reverts to $c(4\times 2)$ by setting the bias voltage negative.⁹ In the following, we show that the $p(2\times 2)$ -to- $c(4\times 2)$ transition induced at negative V_b is highly localized just under the STM tip apex, and that rewritable nanometer-scale patterns can be formed at 80 K.

All the experiments were performed in an ultrahigh vacuum system composed of surface preparation and STM chambers. A commercial variable-temperature scanning tunneling microscope (OMICRON, LT-STM) was installed in the STM chamber. Germanium specimens ($8\times 3\times 0.4$ mm³) were cut from a Sb-doped *n*-type Ge(001) wafer (0.35 Ω cm). *In situ* surface cleaning was accomplished in the preparation chamber by repeated cycles of argon ion bombardment (1 kV and 10 min) and annealing at 980–1000 K and with electrical current through the specimen. STM images were obtained at 80 K with a tungsten tip in a constant current mode.

Figure 2 illustrates how the reconstruction of a Ge(001) surface changes with V_b in the STM observation. At a negative V_b (e.g., -2.0 V), $c(4\times 2)$ reconstruction is realized.

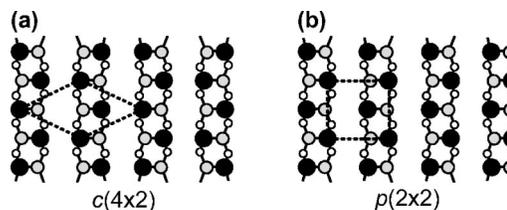


FIG. 1. Arrangement of Ge atoms on (a) $c(4\times 2)$ - and (b) $p(2\times 2)$ -reconstructed Ge(001) surfaces. Large solid circles, open circles, and small open circles denote “up” atoms of buckled dimers, “down” atoms, and Ge atoms in the second layer, respectively. The primitive surface unit cell of each structure is indicated by broken lines. Buckling in adjacent dimer rows is out-of-phase in the $c(4\times 2)$ reconstruction (a), and is in-phase in the $p(2\times 2)$ reconstruction (b).

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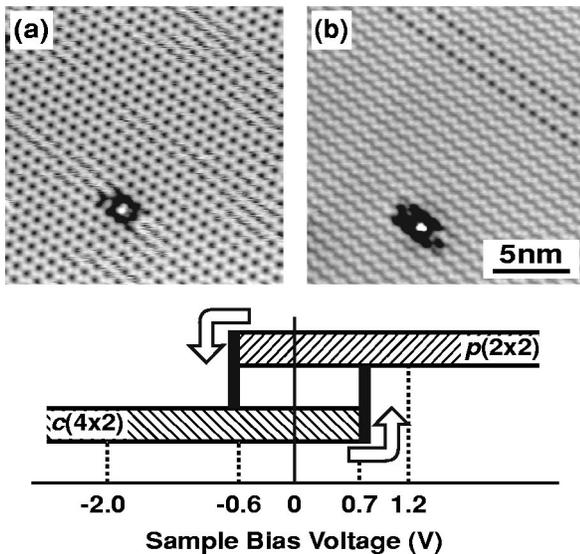


FIG. 2. Dependence of Ge(001) surface reconstruction on sample bias voltage (V_b) in STM observation. STM image recorded at 80 K with $V_b = -2.0$ V exhibits $c(4 \times 2)$ reconstruction (a), whereas that recorded in the same region with $V_b = +1.2$ V exhibits $p(2 \times 2)$ reconstruction (b). When V_b is kept between the negative (approximately -0.6 V) and positive (approximately $+0.7$ V) thresholds, the STM observation does not flip the buckled dimers, and the surface structures are preserved.

Due to the out-of-phase arrangement of buckled dimers in adjacent dimer rows [Fig. 1(a)], the STM image looks honeycomb. When V_b is increased, the $c(4 \times 2)$ structure is unchanged until V_b exceeds a positive threshold voltage around $+0.7$ V. In the STM recording above the threshold, the surface reconstruction changes to $p(2 \times 2)$ gradually dimer row by dimer row. The STM image obtained with $V_b = +1.2$ V shows zigzag lines corresponding to in-phase dimer buckling in the $p(2 \times 2)$ reconstruction [Fig. 1(b)]. Since two $p(2 \times 2)$ domains translated each other by half a period are

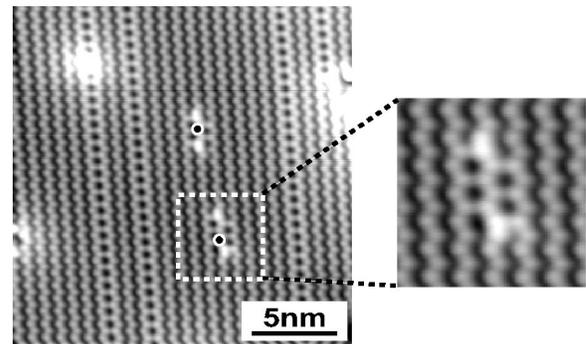


FIG. 3. Small $c(4 \times 2)$ -reconstructed domains formed in the $p(2 \times 2)$ region of a Ge(001) surface. Two negative pulses (-0.8 V, 0.8 nA, and 0.5 s) were applied at the positions denoted by two dots. To avoid the influence on the surface reconstruction, the STM image was recorded with $V_b = -0.2$ V.

equally probable, domain boundaries with local $c(4 \times 2)$ structure run along the dimer rows. The $p(2 \times 2)$ -reconstructed surface is stable until V_b is decreased to a negative threshold voltage around -0.6 V. The negative and positive thresholds correspond to the calculated positions of occupied π and empty π^* bands of the buckled Ge(001) surface.¹⁰ We consider that hole (electron) injection into the π (π^*) band causes the $p(2 \times 2)$ -to- $c(4 \times 2)$ [$c(4 \times 2)$ -to- $p(2 \times 2)$] transition.

We have found that, by setting V_b slightly below the negative threshold, the reconstruction transition from $p(2 \times 2)$ to $c(4 \times 2)$ can be confined to just the vicinity of the point where the current tunnels from the STM tip. While scanning the surface with $V_b = -0.2$ V, we suspended the scan in a $p(2 \times 2)$ -reconstructed region, changed V_b to -0.8 V for 0.5 s, and then resumed the scan with $V_b = -0.2$ V. The effects of the -0.8 V pulse are revealed in the STM image of Fig. 3 subsequently recorded with $V_b =$

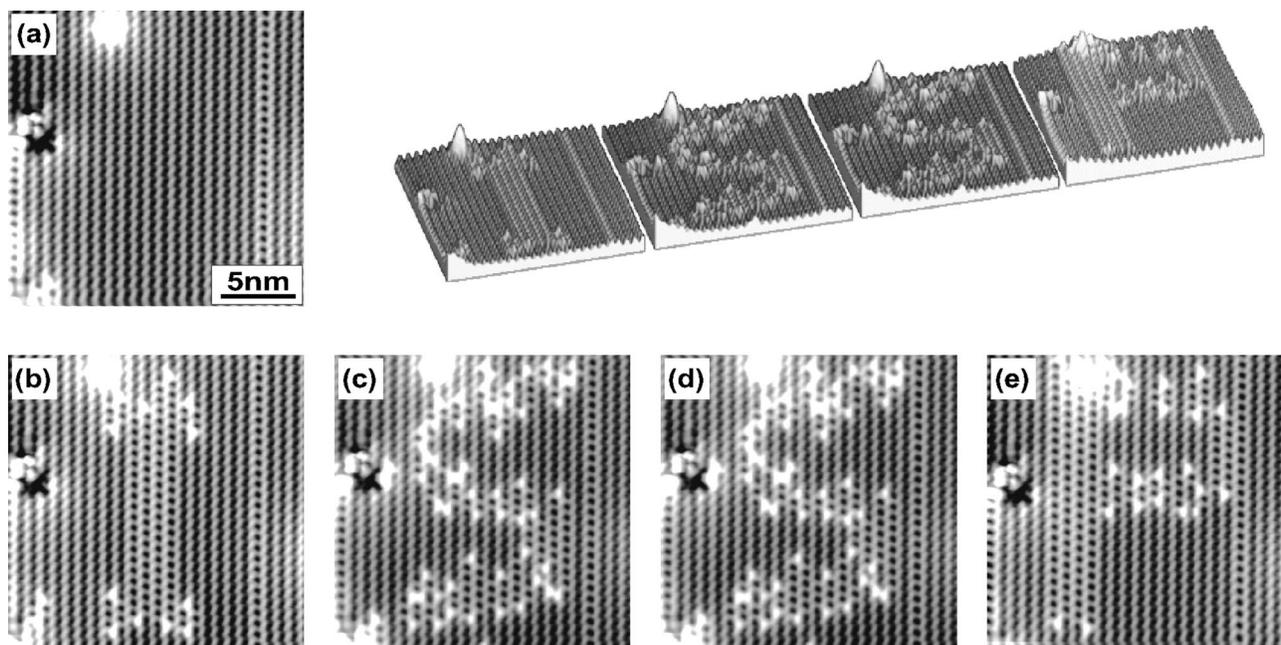


FIG. 4. Rewritable nanometer-scale patterns on Ge(001). In the $p(2 \times 2)$ -reconstructed region (a), three characters, “I” (b), “S” (c), and “P” (e), are sequentially written in the same position by locally flipping dimers to $c(4 \times 2)$ with negative pulses (-0.8 V, 1.0 nA, and 0.5 s). All the STM images were recorded with $V_b = -0.2$ V not to disturb the flipped dimers. The second “S” (d) is just a duplicate of the first one (c); “ISSP” is our institute. Bird’s-eye view is shown on the upper right. At -0.2 V, $c(4 \times 2)$ domains look slightly higher than $p(2 \times 2)$ domains.

-0.2 V. Two dots in the figure indicate the points where the negative pulses were applied. There appear small $c(4\times 2)$ -reconstructed domains centering at the two dots. The domains extend over three dimer rows (1.6 nm in width), indicating that only dimers in the central row have been flipped by the negative pulse. Along dimer rows, the domains extend only over five or six dimers (~ 2 nm in length). By virtue of this confinement of $p(2\times 2)$ -to- $c(4\times 2)$ transition, nanometer-scale patterns can be written on a Ge(001) surface. The performance of our process is demonstrated in Fig. 4 by three characters, “I,” “S,” and “P,” sequentially written in the same position on the Ge(001) surface. [Note that the transition in the reverse direction, i.e., from $c(4\times 2)$ to $p(2\times 2)$, with positive V_b extends along the dimer rows and is not confined to the area scanned by the STM tip.⁹]

Since an initial clean Ge(001) surface exhibits $c(4\times 2)$ reconstruction at 80 K, we first prepared a $p(2\times 2)$ -reconstructed region by scanning the region at a positive V_b (+0.8 V). The surface structure was confirmed by the STM image recorded with $V_b = -0.2$ V [Fig. 4(a)]. A defect on the left-hand side and a domain boundary [a $c(4\times 2)$ wire] running on the right-hand side of the image serve as markers in the following figures.

Then, we wrote “I” in the following way. While scanning the region with $V_b = -0.2$ V, we stopped the scan and changed V_b to -0.8 V to flip the dimers locally to $c(4\times 2)$ arrangement. After 0.5 s, we restarted the scan with $V_b = -0.2$ V. In the following several horizontal scans, we could confirm that the preceding negative pulse had successfully flipped the dimers locally. After the horizontal scanning line moved upward, we stopped the scan at the position in line with the flipped area, and applied the negative pulse again to extend the $c(4\times 2)$ domain. Repeating the negative pulses, monitoring the written pattern with $V_b = -0.2$ V, and erasing the overexpanded $c(4\times 2)$ area with positive pulses, we succeeded in writing the character “I” [Fig. 4(b)].

The character “I” was erased by scanning the whole region with $V_b = +0.8$ V. The region returned to $p(2\times 2)$ reconstruction similar to that shown in Fig. 4(a). On the restored surface, we wrote the characters “S” [Fig. 4(c)], and then “P” [Fig. 4(e)] in a similar manner. The most conspicuous features in these STM images are small bright triangles

scattered at the periphery of each pattern. These correspond to pairs of dimers buckled in the same orientation. Such a pair is not allowed in an alternately buckled dimer row inside the $p(2\times 2)$ -or $c(4\times 2)$ -reconstructed area, but produced at the boundary between $p(2\times 2)$ and $c(4\times 2)$ domains. As evidenced by the positions relative to the markers, these characters are written in the same position. This means that the writing and erasing procedures described above do not degrade the surface and that nanopatterns can be rewritten many times.

Finally, we summarize the characteristics of our nanopatterning process on a Ge(001) surface at 80 K. First, the nanopatterns are rewritable since the process is based on the physical change. It does not contain any irreversible chemical reactions. Second, writing, recording, and erasing nanopatterns are carried out at liquid nitrogen temperature. Although it is still below room temperature, liquid nitrogen temperature is rather easy to access. This point seems important practically. Third, the writing procedure is very simple, just adjustment of the sample bias voltage during a STM scan. Written patterns can be monitored in the following STM image recording at a small V_b . Moreover, correction of the patterns is accomplished by recovering locally $p(2\times 2)$ arrangement with a positive pulse. Thus, by switching V_b back and forth, we can write, check and correct the nanopatterns *in situ* easily. Though it is at a very primitive stage, a Ge(001) surface seems to have basic characteristics which are required to realize rewritable nanometer-scale memory on it.

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