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Structural transformation of Ge dimers on Ge(001) surfaces induced by bias voltage*

Qin Zhi-Hui(秦志辉), Shi Dong-Xia(时东霞), and Gao Hong-Jun(高鸿钧)†

Nanoscale Physics & devices Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, *China*

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Scanning tunnelling microscopy is utilized to investigate the local bias voltage tunnelling dependent transformation between (2×1) and c(4×2) structures on Ge(001) surfaces, which is reversibly observed at room temperature and a critical bias voltage of −0.80 V. Similar transformation is also found on an epitaxial Ge islands but at a slightly different critical bias voltage of −1.00 V. It is found that the interaction between the topmost atoms on the STM tip and the atoms of the dimers, and the pinning effect induced by Sb atoms, the vacancies or the epitaxial clusters, can drive the structural transformation at the critical bias voltage.

Keywords: scanning tunnelling microscopy, surface structures, Ge, structural transition
PACC: 6116P, 6820, 6855, 6842

1. Introduction

The group IV elements surfaces, especially the (001) surfaces, play a major role in scientific researches and technological applications due to various effects of self-organization, and provide a launching platform for the solid state electronic evolution.[1−4] Among these surfaces, more and more interests have been focused on Ge (001) surface, because it has potential applications in semiconductor industry and is quite similar to the well-studied Si (001) surface in many aspects.[1,5,6] On Ge (001) surface, every two atoms form a dimer which tilts from the surface plane; and the Ge dimers align in the [110] direction, forming dimer rows. There are three kinds of reconstructions on Ge(001) surfaces. The neighbouring dimers in the same dimer row alternatively buckle, resulting in two higher-order reconstructions, p(2×2) structure (the buckling orientation of the dimers standing side by side on adjacent dimer rows is the same) and c(4×2) structure (opposite). The third reconstruction is (2×1) structure, which consists of rapid flip-flop dimers exhibiting symmetric appearance.[7] Among them, structural transformations have been reported with the help of the variable temperature scanning tunnelling microscopy (STM). Kevan found a structural transition from c(4×2) to (2×1) on Ge (001) surface occurring at 220–260 K.[8] It was also reported by Zandvliet *et al* that the c(4×2) to (2×1) transition on Ge(001) surface occurred just below room temperature,[9] and at room temperature Ge (001) surface presented ordered striped pattern of (2×1) and c(4×2),[10] which was explained by relaxation theory.[11] Structural transition between (2×1) and c(4×2) is well known to take place in the temperature range from room temperature to 200 K because the flipping motion of Ge dimers at room temperature is stabilized (frozen) at low temperatures. Scanning tunnelling microscopy is used not only to study the atomic and molecular structures but also to manipulate the atoms and molecules; structural transitions induced by scanning bias voltage in electrical bistable molecular systems have been investigated widely in the area of nano-electronic devices.[12] Takagi *et al* [13] also reported a reversible transformation between c(4×2) and p(2×2) on clean Ge (001) surface occurring below 80 K and suggested that it was due to the tunnelling electrons and topological defects.

In the present paper, we focus on the room temperature local structural transformation between c(4×2) and (2×1) structures on Ge (001) surface, which is reversible and induced by sample bias voltage. This phenomenon also occurs on epitaxial Ge islands on Ge (001) surface, but at a slightly higher critical

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†Corresponding author. E-mail: hjgao@aphy.iphy.ac.cn

bias voltage. We try to explain the transformation mechanism and propose a model for this phenomenon.

2. Experimental details

The experiments were carried out in an OMICRON STM apparatus operated in an ultra high vacuum (UHV) chamber with a base pressure of $\sim 5\times10^{-11}$ mbar (1 bar = 10^5 Pa).[14–16] An n-type Sb doped samples with a size of $12\times6\times0.38\,\mathrm{mm}^3$ was cut from a Ge (001) wafer with a room temperature resistivity of $0.4\,\Omega\cdot$cm. After repeated rinse in reagent grade ethanol and subsequently in deionized water, it was introduced into the UHV chamber. Tantalum was used to contact the sample as the heating electrodes for avoiding diffusion during high-temperature treatments. A typical Ge(001) surface preparation cycle included Ar ion bombardment at a current density of $4.2\,\mu\mathrm{Acm}^{-2}$ for 15min plus subsequent annealing at 800±20°C for 10 min. Six cycles were adopted to prepare clean Ge (001) surface. The prepared Ge (001) surface was well characterized by low-energy electron diffraction (LEED) and STM. After that, sub-monolayer Ge was epitaxially deposited on Ge(001) surface using a commercial evaporator (Focus EFM3) with an integral flux monitor. The detailed experimental setup and preparation process had been demonstrated elsewhere.[6,17] The bias voltage-dependent structural transformations both on clean Ge (001) surface and the epitaxial Ge islands were investigated individually. All STM images were recorded at room temperature in constant current mode using an electrochemically etched tungsten tip and the bias voltage was applied to the sample.

3. Results and discussion

As shown in Fig.1, on Ge (001) surface a certain region is repeatedly scanned at different sample bias voltages. In the filled-state images (Fig.1(a)–1(c)), some bright features can be resolved, which appear as depressions in the empty-state image (Fig.1(d)). Under negative sample bias voltage condition, these features can easily give electrons presenting protrusions-like but hardly accept electrons, showing darkness in empty-state image. These features are correlated with the doped Sb elements, which diffuse to the surface due to high temperature annealing, because after bonding with neighbouring Ge atom and forming Sb–Ge dimer, every Sb atom has one pair valence electrons left and can easily give out electrons under negative bias voltage condition. As shown in Fig.1(a), all the dimers are symmetric forming (2×1) structure. On setting the sample bias voltage at −0.80 V (Fig.1(b)), the dimer rows, on which the Sb atoms reside, have a structural transformation from (2×1) to c(4×2) structure. Additionally, on each dimer row the closer the dimers to the Sb atoms, the more the dimers tilting. Further setting the bias voltage to −1.30 V (Fig.1(c)), no additional buckled dimers appear. So it can be concluded that the critical bias voltage for (2×1) to c(4×2) structural transformation is −0.80 V, which is further verified by another experimental result below.

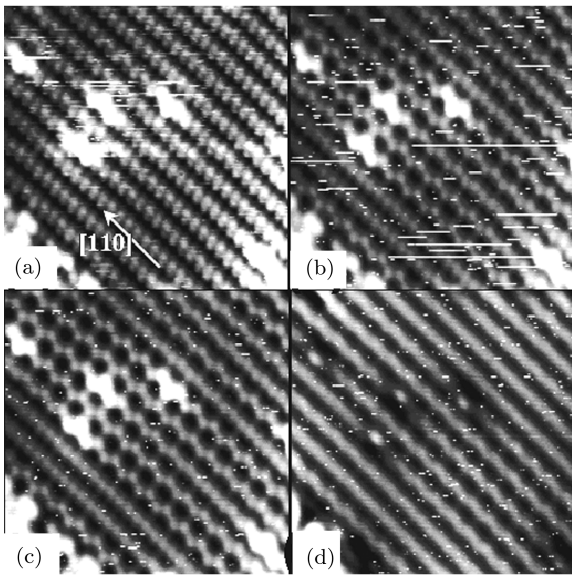


Fig.1. Successive constant-current (0.30 nA) STM images of the same region ($9\times9\,\mathrm{nm}^2$) on Ge(001) surface. The sample bias voltage was −0.40 V (a), −0.80 V (b), −1.30 V (c) and 1.30 V (d).

Figure 2 (left) shows the STM image of another position on the same sample as that in Fig.1. One region marked by a dashed square is successively scanned with different bias voltages as shown in the right panel of Fig.2. The above studies have shown that (2×1) to c(4×2) structural transformation occurs at bias voltage of −0.80 V, so we repeatedly scan this region using bias voltages around −0.80 V. As the bias voltage increases from −0.75 V to −0.85 V, the dimer rows near the protrusions or vacancies in the lower left and the upper right of the region transform from (2×1) to c(4×2). No more dimer rows transform with fur-

ther increasing the voltage to −0.90 V. With the bias voltage decreasing to −0.70 V, the domains exhibiting c(4×2) structure reversely transform to (2×1) structure. Again increasing the bias voltage to −0.80 V, the structural transition occurs repeatedly. The experimental results (Figs.1 and 2) demonstrate that the critical bias voltage is −0.80 V for the substrate structural transformation between (2×1) and c(4×2) structures.

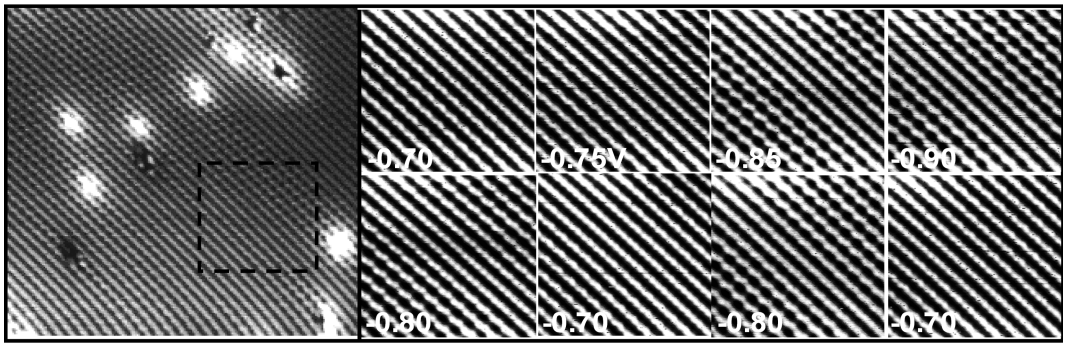


Fig.2. (left) STM image (30×30 nm^2, $V_{\rm bias} = -1.00$ V, $I_{\rm t} = 0.50$ nA) of the Ge(001) surface. The region (9×9 nm^2) identified by a dashed square is successively scanned and shown in the right panels taken at the sample bias voltages indicated in the corresponding images. The eight images were all taken with a tunnelling current of 0.34 nA.

It has been known that c(4×2) structure corresponds to the ground state of Ge (001) surface, and the transformation from c(4×2) to (2×1) structure occurs at 220–260 K.[8] At room temperature, because of thermal fluctuation, the dimers have rapid flip-flop motions exhibiting (2×1) structure as schematically shown in Fig.3(a). During the flip-flop motion of the dimers, there is charge transfer from the lower atoms to the higher ones, so the upper atoms are negatively charged and the lower positively.[18] Schematically shown in Fig.3(b) are two instantaneous states of the relative buckling orientation between the adjacent dimers standing side by side in the neighbouring rows. The upper negatively charged atom of one dimer is close to the upper atom or to the lower positively charged atom of its adjacent dimer. When the substrate is a negatively biased one, there is negative electric field described by Seino *et al.*[19] In this case, the attractive (repulsive) force interacts between the topmost atoms of the tip and the upper (lower) atoms of the dimers. With the increase of the bias voltages, the tip-atoms interaction increases and the dimer tilting state increases. During the scanning of a bias voltage of −0.80 V, the tip-atoms interaction can overcome the flip-flop motion of the Ge-Ge dimers to form buckled ones. The protrusions (Sb atoms) or vacancy defects pin the buckled states of their adjacent Ge-Ge dimers, so only the dimer rows, on which the Sb atoms or vacancies reside, stabilize into asymmetric ones. As reported by Takagi *et al*, the underlying atoms below the upper atom of a buckled dimer were pulled closer while those under the lower ones were pushed apart.[12] The lattice of subsurface in the c(4×2) structure was less distorted than the one in the p(2×2) structure.[12] So the (2×1) structure near the Sb atoms or vacancies has a tendency to transform to c(4×2) structure rather than to p(2×2) structure. On the other hand, when the bias voltage changes from −0.80 V to −0.70 V, the

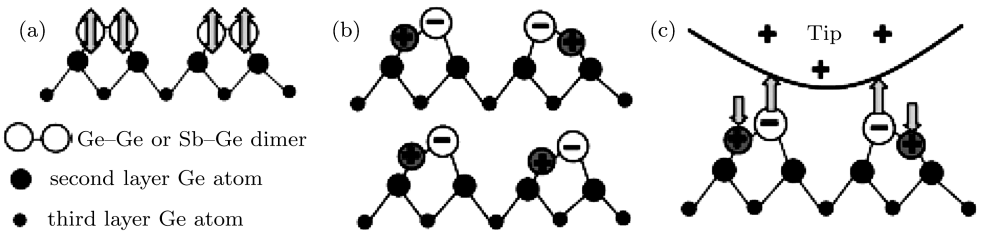


Fig.3. (a) A side view of the (2×1) structure indicating the flip-flop motion. (b) Two instantaneous states of the buckled orientation of the adjacent dimers. (c) Tip-atoms interaction.

tip-atoms interaction decreases and cannot overcome the thermal flip-flop fluctuation. Therefore, the c(4×2) structure transforms to (2×1) structure again. When the substrate is positively biased, there are repulsive (attractive) forces between the tip atoms and the upper (lower) atoms of the dipoles. So the dimers tend to exhibit symmetric state as shown in Fig.1(d).

A similar transformation also occurs at the epitaxial Ge islands on Ge (001) surface but with different critical voltages. As reported by Galea *et al*[20] and Li *et al*,[21] on Ge(001) surface, at lower epitaxial Ge coverages (below 0.12ML), the C dimers and clusters of C dimers (CC clusters) are dominant on the surface. Here, one monolayer (ML) is equal to 6.24×10^{14} atoms/cm^2 and is the number density of sites for the unreconstructed Ge(001)-1×1 surface. Figures 4 (a) and 4(b) show the empty-state and the filled-state STM images of homogeneously epitaxial Ge growth on Ge(001) surface, respectively. The Ge clusters were grown by deposition of 0.15 ML Ge at 400 K and then annealed at 450 K for 1 h. The smallest species are the epitaxial Ge dimer row consisting of two dimers. No isolated Ge monomers are distributed on the surface; the longest epitaxial dimer row consisting up to eight dimers can also be seen. All the epitaxial Ge dimer rows orientate themselves perpendicular to the substrate dimer rows. Figure 4(c) shows 0.20 ML Ge deposited at 450 K and annealed at 510 K for 1h. A larger island made up of ten dimer rows with the longest one consisting more than twenty dimers is observed.

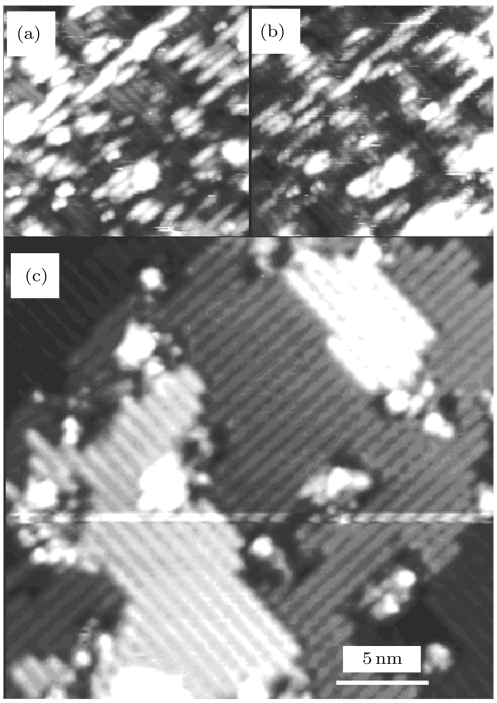


Fig.4. (a) Empty-state (0.55 V) and (b) filled-state (−0.55 V) STM images of the same area (20×20 nm^2) obtained after 0.15ML Ge was deposited at 400 K and annealed at 450 K for 1h. The tunnelling current for the two images was set at 0.34 nA. The dimers on some epitaxial dimer rows can be differentiated in (b), and are perpendicular to the substrate dimer rows. (c) STM image (27×27 nm^2, $V_{\rm bias} = 1.27$ V, $I_{\rm t} = 0.37$ nA) of 0.20 ML Ge deposited on Ge(001) surface at 450 K and annealed at 510 K for 1 h.

To gain insight into the transformation of the epitaxial dimers on Ge (001), the smaller island on the upper right of Fig.4(c) is repeatedly scanned with different sample bias voltages. Time lapse between the two images is about 4 minutes. Figure 5 shows the successive STM images with the bias voltages indicated in corresponding images, which exhibit local-bias-voltage-dependent structural transformation. At high negative bias voltages, the entire epitaxial dimers exhibit the buckled state due to the STM tip interaction with the atoms of dimers, and the pinning effect of the irregular clusters on the two sides of the row, which have strong pinning effect as C dimers or CC dimers.[20] It is noted that the dimers on the lower right section of the third dimer row begin to change from buckled state to unbuckled state as the bias voltage changes from −1.70 V to −1.00 V. Therefore, the critical bias voltage is −1.00 V, which is a little higher than that for the structural transition on the substrate surface. In addition, the number of the buckled dimers that

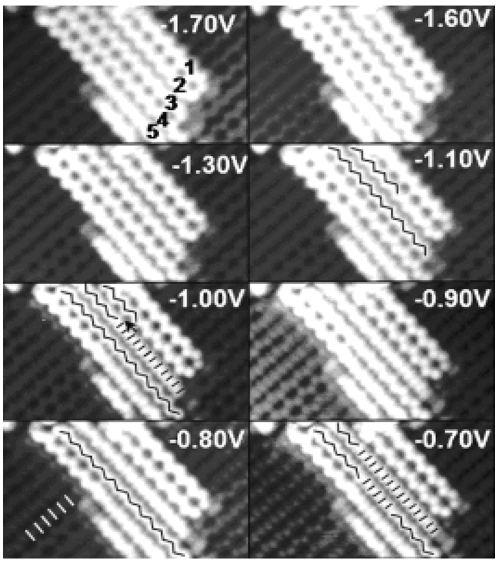


Fig.5. Variation of consecutive filled-state STM images of the same area (9×8 nm^2) with sample bias voltages indicated in each image. These images show the bias voltage-dependent changes of local structure and are all recorded at a tunnelling current of 0.47 nA.

transform to unbuckled ones increases with the decrease of the absolute value of bias voltage.

This transformation process can be described as follows. The interaction between the epitaxial Ge dimers and the underlying surface Ge dimers is weaker than that between the surface Ge dimers and the subsurface ones. So the flip-flop motion of the epitaxial Ge dimers is more active. As the bias voltage changes to $-1.00\,\mathrm{V}$, the tip-atoms interaction cannot prevail over the thermal fluctuation of some buckled epitaxial Ge dimers, which transform into unbuckled state. On further decreasing the absolute value of bias voltages, the weaker the tip-atoms interaction, the more the epitaxial buckled Ge dimers (as shown in the third and fourth dimer rows) overcome the interaction and transform to the unbuckled state. Due to the strong pinning effect of the irregular clusters, some of the epitaxial dimers, such as those on dimer rows 1 and 2, still maintain the buckled state even at lower bias voltages. With the bias voltage changing to $-1.10\,\mathrm{V}$, the dimers exhibiting (2×1) structure reversely transform to c(4×2) structure. It is supposed that the critical bias voltage for the structural transformation on epitaxial Ge islands is influenced by the size of the islands and the distribution of epitaxial clusters on periphery of the islands. In general, the larger the islands, the lower the absolute value of critical bias voltages for transformation, which should be close to, but higher in absolute value than $-0.8\,\mathrm{V}$. Meanwhile, the local transformation of substrate structures is also observed. As the bias voltage changes from $-0.80\,\mathrm{V}$ to $-0.70\,\mathrm{V}$, the dimers on one dimer row in the lower left of the scanning region begins to transform from c(4×2) to (2×1) structure, which is identical with the results shown in Figs.1 and 2.

4. Conclusions

We have demonstrated the local bias voltage dependent transformation between (2×1) and c(4×2) structures on Ge (001) surface at room temperature. The critical bias voltage for this reversible transformation is $-0.80\,\mathrm{V}$. A similar structural transformation is also revealed on an epitaxial Ge island but at a critical bias voltage of $-1.00\,\mathrm{V}$, a little higher in absolute value than that for the substrate structural transformation. A simple transformation model is proposed and the transformation mechanism is also discussed. As a consequence, this kind of structural transformation is driven by the interaction between the topmost atoms on the STM tip and the atoms of the dimers, together with the pinning effect induced by Sb atoms, the vacancies or the epitaxial clusters.

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