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Energy barrier for dimer flipping at the Si(001)-(2×1) surface in external electric fields

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Effects of external electrostatic fields, $\mathbf{E}_{\text{ext}}$, on a barrier in energy for dimer flipping, E_{B}, at the Si(001) -(2×1) surface have been investigated using first-principle total energy calculations. It has been revealed that E_{B} changes in proportion to $\mathbf{E}_{\text{ext}}$. This finding suggests that we can turn on and off the flip-flop motions by alternating the polarity of the field with a scanning tunneling microscope (STM) at low temperatures, which is consistent with the recent experimental results. It has also been shown that the $c(4\times2)$ surface is more stable than the $p(2\times2)$ even in electric fields typical of STM experiments.

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A large number of scanning tunneling microscopy (STM) experiments have revealed structural and electronic properties of various surfaces so far. In the STM configuration, a strong electric field is applied between a tip and a surface to observe atomic structures at surfaces. Therefore, much interest has been devoted to effects of the electric field on structural and electronic properties of surfaces both experimentally[1–3] and theoretically.[1,4–12] However, such electric fields have not been regarded as an important factor for investigating the atomic configuration at clean surfaces under the condition typical of STM observations. For example, the electronic structure of the Si(001) clean surface is only weakly perturbed and the atoms at the surface are displaced by only a few hundredths of an angstrom.[4–6]

Recently, two groups have reported the bias-assisted manipulation of the surface reconstruction: Takagi *et al.* have reported that the surface reconstruction on Ge(001) is locally and reversibly changed between $c(4\times2)$ and $p(2\times2)$ by controlling the sample bias voltage of STM, V_s, below 80 K.[13] They have also observed bistability phenomena between $c(4\times2)$ and $p(2\times2)$ depending on V_s and the tunneling current. On the other hand, Sagisaka *et al.* have demonstrated the phase manipulation between $c(4\times2)$ and $p(2\times2)$ on Si(001) at 4.2 K through a flip-flop motion of the buckling dimers at the surface under a control of V_s.[14] Stimulated by their experiments, we re-illuminate effects of the electric field on atomic configurations of clean surfaces. In particular, we report on changes of a barrier in energy for dimer flipping at Si(001) with homogeneous, external electrostatic field perpendicular to the surface, using first-principles calculations with the density functional theory. Interestingly, it has been revealed that the energy barrier for dimer flipping is significantly lowered under positive V_s conditions as suggested experimentally by Sagisaka *et al.*,[14] even while the $c(4\times2)$ structure remains to be energetically favored with compared to the $p(2\times2)$ in electric fields typical of STM experiments.

We performed first-principles total energy and band calculations[15] based on the density functional theory[16,17] by using the norm conserving pseudopotential suggested by Troullier and Martins.[18] Exchange and correlation were treated with a local density approximation.[19,20] The wave functions were expanded in a plane-wave basis set with a kinetic-energy cutoff of 25 Ry. Brillouin zone integration was done at 64 K points in the (1×1) two-dimensional zone, and structures were optimized with the use of a conjugate gradient method.

A repeated slab geometry was used for the simple calculation, which has a supercell consisting of 9 ML of Si and of a vacuum region corresponding to about 7 ML in thickness. The backside of the slab was terminated with H atoms that eliminate artificial dangling bonds and prevent it from coupling with the front side.

In order to apply an external electrostatic field perpendicular to the surface of the slab, we introduce a planar dipole layer in the middle of the vacuum region.[21–24] As a result of the introduction of the dipole layer, a following dipole potential in cgs Gaussian system of units,

$$v^{\text{dip}}(z) = -e\left(\frac{4\pi m_z}{c_0} - E_{\text{ext}}\right)z, \tag{1}$$

is added to the conventional periodic potential, $v^{\text{per}}(\mathbf{r})$, where c_0 is the height of the supercell perpendicular to the surface along the z axis, m_z the electric dipole moment per unit area. The domain of definition for z is specified by $-c_0/2 < z < c_0/2$. Here, we have to calculate m_z self-consistently on the basis of the charge density of the slab. A finite value of m_z without the external field corresponds to the spontaneous polarization of the slab employed. We calculate the total energy of a system in external electric fields as follows:

$$E_{\text{tot}} = E_{\text{tot}}^{\text{per}} + \left(\frac{2\pi m_z}{c_0} - E_{\text{ext}}\right)Am_z, \tag{2}$$

where $E_{\text{tot}}^{\text{per}}$ is the total energy calculated on the periodic potential and A is the area of the surface unit cell.

In optimizing atomic configurations of the slab in external electric fields, the atoms in the back side H layer and its adjacent 2 ML of Si were fixed and those in the front side 7 ML were allowed to relax on the basis of the Hellmann-Feynman force,

$$\mathbf{F}_I = \mathbf{F}_I^{\text{per}} - eZ_I\left(\frac{4\pi m_z}{c_0} - E_{\text{ext}}\right)\hat{z}, \tag{3}$$

where $\mathbf{F}_I^{E_{\text{ext}}=0}$ is the Hellmann-Feynman force calculated with

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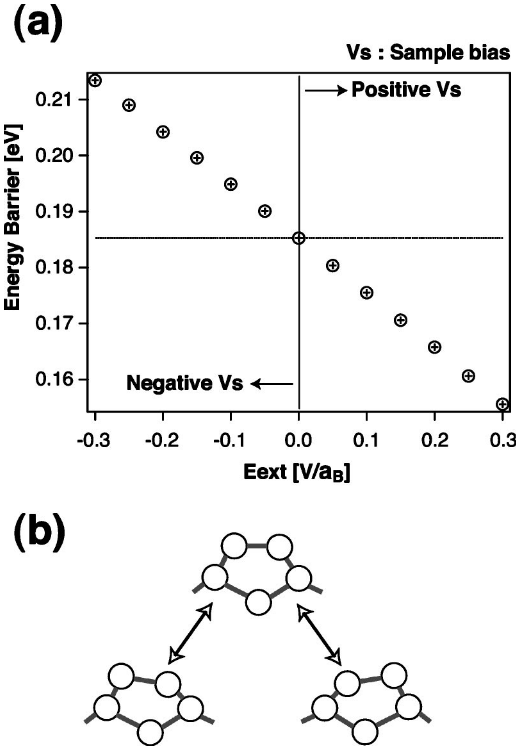

FIG. 1. (a) Electric field dependence of the energy barrier for flipping the buckled dimer between two possible orientations, (b). Negative electric fields correspond to negative sample biases, and vice versa.

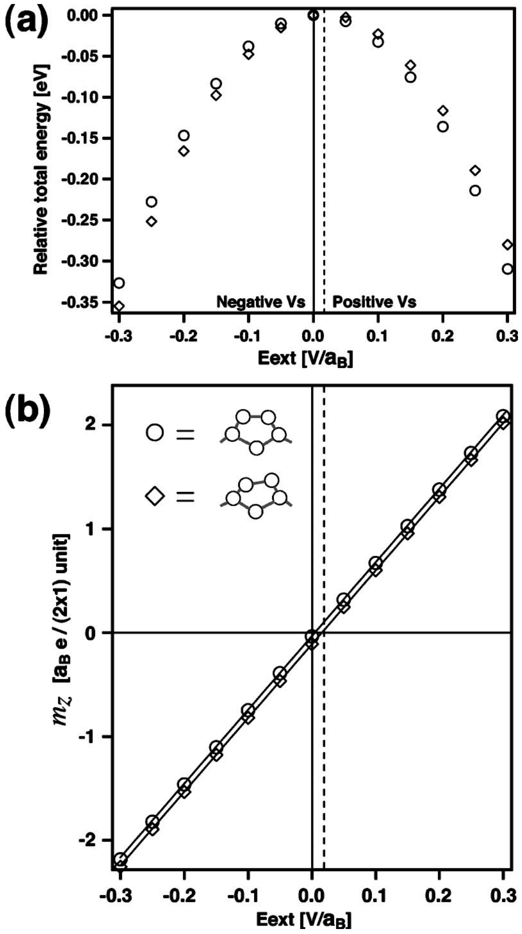

FIG. 2. (a) Deviations of the total energy in electric fields from that in zero external field for the symmetric dimer model (○) and the asymmetric one (◇), and (b) absolute values of the electric dipole moment perpendicular to the surface per (2×1) unit cell, as a function of E_{ext}. Vertical broken line shows the symmetry axis for the asymmetric dimer surface.

regard to the periodic potential, $v^{\text{per}}(\mathbf{r})$, Z_I the ionic charge of ion I, and $\hat{z}$ the unit vector along the z direction.

Figure 1 shows the energy barrier for dimer flipping, E_{B}, at the Si(001)-(2×1) surface as a function of the external electric field, E_{ext}. Here, the negative value of E_{ext} corresponds to the negative sample bias, and vice versa; that is, the positive direction of E_{ext} points out of the surface. We can see that the energy barrier changes in proportion to the external electric field and is lowered at positive sample biases; $\Delta E_{\text{B}}=-19$ meV for $E_{\text{ext}}=0.2\ \text{V}/a_{\text{B}}$. This tendency is consistent with the recent experiments at 4.2 K; the flip-flop motions do not occur at a lower bias voltage below $V_s=+1.0$ V but do at a higher *positive* voltage ($\sim+1.5$ V).[14] Therefore, we can say that such a field effect is one of a root for the frequent excitation of flip-flop motions.

Figure 2(a) shows deviations of the total energy of the slab with the external field from that without the external field, ΔE_{total}, as a function of E_{ext}. As seen in this figure, ΔE_{total} changes quadratically. Here, it is noteworthy that ΔE_{total} for the symmetric dimer surface seems to be symmetric with respect to the polarity of external fields, while that for the asymmetric one is symmetric not with respect to $E_{\text{ext}}=0$ but with respect to the electric field at which m_z is quenched. In other words, the maximum of E_{total} for the asymmetric dimer surface is shifted; the vertical broken line shown in Figs. 2(a) and 2(b). This is due to the difference in the net dipole moment normal to the surface without the external field, as shown in Fig. 2(b), -0.037 and $-0.110\ a_{\text{B}}\cdot e/(2\times1)$ for the slabs having the symmetric and the asymmetric dimer surfaces, respectively. This figure also shows that the electric dipole moment perpendicular to the surface changes linearly with the field applied within the range from -0.3 to $+0.3\ \text{V}/a_{\text{B}}$, namely,

$$m_z = m_z^{E_{\text{ext}}=0} + cE_{\text{ext}}, \tag{4}$$

where c corresponds to the polarizability constant for slabs.

Next, in order to qualitatively answer the question of what causes the change of the energy barrier for dimer flipping, E_{B}, we focus our attention to the dipole moment at the surface dimer. Since the dimers are tilted in the asymmetric configuration, the up (down) atom has an s-like (p-like) dangling bond, which results in a larger (smaller) orbital electronegativity of the dangling bond of the up (down) atom, respectively.[25–27] Therefore, the buckling of dimers brings about charge transfer from the down atom to the up one,[28] inducing a certain amount of the dipole moment perpendicular to the surface, as schematically shown in Fig. 3. The absolute value of this dipole moment originated from the buckling is evaluated as the difference between the total dipole moments for the symmetric and asymmetric dimer mod-

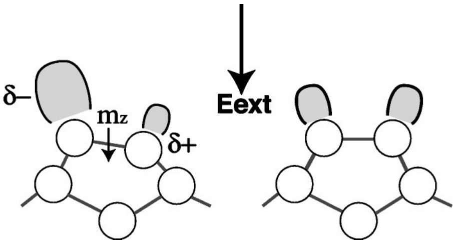

FIG. 3. Schematic illustrations of the surface dipole at the asymmetric dimer.

els, $\delta m_z^{E_{\text{ext}}=0} = |m_z^{\text{asym}} - m_z^{\text{sym}}| = 0.073\ a_{\text{B}} \cdot e/(2\times 1)$ for $E_{\text{ext}}=0$ from Fig. 2(b). This can be regarded as the *intrinsic* dipole moment for the asymmetric dimer surface. Because this dipole is stabilized in negative electric fields shown in Fig. 3, the energy barrier for dimer flipping lowers in positive electric fields. Here, it must be noted that the change in the intrinsic dipole moment induced by the electric field at the surface is small over a range of external fields from $-0.3\ \text{V}/a_{\text{B}}$**(**$0.067\ a_{\text{B}} \cdot e/(2\times 1)$**)** to $+0.3\ \text{V}/a_{\text{B}}$ (0.072). These results are consistent with the fact that the optimized tilt angle of the dimer remains almost unchanged; 18.0°, 17.5°, 17.0° for −0.3, 0.0, +0.3 V/a_{B}, respectively. Viewed in this light, it is indicated that the change in energy barrier for dimer flipping, ΔE_{B}, is simply associated with the intrinsic dipole moment of the asymmetric dimer, $\delta m_z^{E_{\text{ext}}=0}$, and the external field, that is,

$$\Delta E_{\text{B}} \sim E_{\text{ext}} \delta m_z^{E_{\text{ext}}=0}. \tag{5}$$

Finally, we have to discuss if the relative energy between the $p(2\times 2)$ and the $c(4\times 2)$ surfaces changes as a function of external fields. Figure 4 shows the difference in total energy per (2×1) between the $p(2\times 2)$ and the $c(4\times 2)$ surfaces. Here, negative values prefer to form the $c(4\times 2)$ surface. It is clearly addressed that the relative stability between these surfaces is hardly affected by external electric fields; the surface still prefers to form the $c(4\times 2)$ structure under the external field from −0.3 to $+0.3\ \text{V}/a_{\text{B}}$. This tendency does not accord qualitatively with the other work.[29] As is the case with the (2×1) surface, the structural parameters remain almost unchanged in external fields; the optimized tilt angles of the dimer of the $c(4\times 2)$ $[p(2\times 2)]$ surface are 19.1° (19.0°), 19.0° (18.9°), and 18.9° (18.8°) for −0.1, 0.0 +0.1 V/a_{B}, respectively. These results agree well with other theoretical ones, e.g., Refs. 4–6 and 29. On the other hand, the difference in dipole moment of slabs between the $p(2\times 2)$ and the $c(4\times 2)$ surfaces, $\Delta m_z = m_z^{c(4\times 2)} - m_z^{p(2\times 2)}$, for $E_{\text{ext}}=0$ is very small and also hardly changes with electric fields; $\sim +0.002\ a_{\text{B}} \cdot e/(2\times 1)$ over the range from −0.1 to $+0.1\ \text{V}/a_{\text{B}}$, being consistent with the fact that the atomic arrangement at the surface remains almost unchanged with electric fields. This is the main reason why the $c(4\times 2)$ surface remains to be more stable than the $p(2\times 2)$ even in electric fields. Here, the positive sign of Δm_z results from negatively larger dipole moment at the $p(2\times 2)$ surface than the $c(4\times 2)$, reflecting the fact that interactions between dipoles at the surface prefer the $p(2\times 2)$ arrangement.[30]

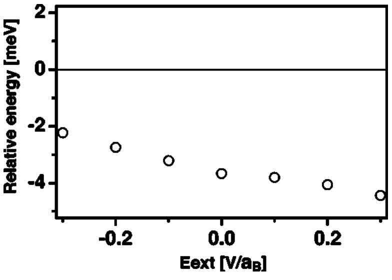

FIG. 4. Relative energy per dimer between the the $p(2\times 2)$ and the $c(4\times 2)$ surfaces, $E^{\text{relative}}_{\text{tot}/(2\times 1)} = E^{c(4\times 2)}_{\text{tot}/(2\times 1)} - E^{p(2\times 2)}_{\text{tot}/(2\times 1)}$.

It has been assumed in our calculations that all dimers flip synchronously. This situation is surely not what happens in actual experiments where dimers flip mostly individually or possibly in small groups. On the other hand, Hwang *et al.* have suggested the energy barrier for concurrent flip-flip motions becomes higher than that for individual ones.[31] As shown in Eq. (5), however, it is obvious that the change of the energy barrier for dimer flipping in external fields is originated from the intrinsic dipole moment existing on an asymmetric dimer. Further, the intrinsic dipole moments for the (2×1) asymmetric dimer, $c(4\times 2)$, and $p(2\times 2)$ surfaces are almost the same, +0.073, +0.052, and $+0.054\ a_{\text{B}} \cdot e/(2\times 1)$, respectively. This means that the order of ΔE_{B} determined by Eq. (5) has little dependence on arrangements of asymmetric dimers at Si(001). Thus, we can say qualitatively that positive electric fields do lower the energy barrier in flip-flop motions, even if quantitative dependence of the energy barrier on external fields remains matter for debate. On the other hand, Sagisaka *et al.* have also suggested that the flip-flop motion initiates the phase transition between the $c(4\times 2)$ and the $p(2\times 2)$ surfaces.[14] These results lead to a possibility that the onset of the flip-flop motions with positive external fields is one of the trigger of the phase transition between the $c(4\times 2)$ and the $p(2\times 2)$ surfaces, although the Si(001) surface still prefers to form energetically the $c(4\times 2)$ structure rather than the $p(2\times 2)$ at least within a range of external fields from −0.3 to $+0.3\ \text{V}/a_{\text{B}}$, which are typical conditions of STM experiments. However, there is room for further investigation with regard to other mechanisms like current effects, proximity ones, or dynamical ones. More experimental, as well as theoretical, work on the phase transition is needed.

In summary, on the basis of the first-principles total energy calculations, we have demonstrated the external electrostatic field dependence of the energy barrier for dimer flipping at the Si(001)-(2×1) surface. It has been shown that the energy barrier for dimer flipping lowers with use of the positive external electric field, namely, positive V_s. This is mainly due to the energetics of the surface dipole moment attributed to the asymmetric dimer configuration in external electric fields. These findings indicate that we can turn on and off the flip-flop motions by alternating the field with an STM at low temperatures, which is indeed consistent with the experimental results. On the other hand, it has also been revealed that the Si(001) surface prefers energetically the

$c(4\times2)$ structure rather than the $p(2\times2)$ even in electric fields. On these grounds, we arrive at the conclusion that the phase manipulation between $c(4\times2)$ and $p(2\times2)$ on Si(001) with STM is not attributed to the static energetics in external electrostatic fields.

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