Ordering of dimer vacancies on the Si(100) surface

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We have investigated the ordering of dimer vacancies, in particular the formation of dimer-vacancy line defects, on the Si(100) surface using a tight-binding total-energy approach. We find that the dimer-vacancy line formed perpendicular to the direction of the surface dimer row is energetically favorable at low vacancy concentrations, whereas at higher vacancy concentrations the dimer-vacancy line is aligned parallel to the direction of the surface dimer row. The energetics and geometries of various dimer-vacancy configurations and the possible pathways to the line-defect formation through the diffusion of dimer vacancies are discussed. The calculated results are in good agreement with experiments and provide an explanation for the observed structural transition resulting from a temperature-driven random-ordered dimer-vacancy redistribution. [S0163-1829(99)07435-4]

I. INTRODUCTION

The Si(100) surface has been extensively studied for decades due to its interesting surface reconstruction and its wide applicability to device fabrications. Recent high-resolution scanning tunneling microscopy (STM) images of the Si(100) surface have shown that single missing dimers are the dominant defect structure at the surface. A higher concentration of random dimer defects can be generated by removing individual atoms from the surface using the ion sputtering technique, yielding multiple missing dimers such as craters of missing dimers. An interesting observation is that with annealing of the highly defected surface at 600 °C, the randomly distributed dimer vacancies migrate to form line defects perpendicular to the surface dimer rows, although the starting Si(100)-(2×1) surface was remarkably free from any metal contamination which could give rise to line defects. Annealing at higher temperatures of 750 and 850 °C for 2 min has produced the same effect as the annealing at 600 °C for 2 min. However, annealing at 950 °C for 2 min or just flashing to 1200 °C for a few seconds has completely restored the random defect distribution. Meanwhile, no ordering of the dimer vacancies was observed when the surface was annealed at 500 °C for 2 min, implying that the transition temperature for the observed ordering of dimer vacancies on the Si(100) surface is between 500 and 600 °C.

Most recently, Zandvliet reported a more systematic study of the temperature-driven ordering of dimer vacancies on the Si(100) surface at various dimer vacancy densities, and showed that, when annealed at the same temperature range as previously reported, the dimer vacancy line is aligned perpendicular to the direction of the surface dimer row for dimer-vacancy densities less than 0.3 monolayers (ML), whereas the equilibrium vacancy line structure is rotated by 90°, that is, aligned parallel to the surface dimer row, for higher dimer-vacancy densities.

These experimental results suggest that there exists a temperature-driven structural transition of the dimer vacancy distribution on the Si(100) surface, and the ordered dimer vacancy structures only exist in an intermediate temperature range. An evaluation of the energetics of various dimer vacancy configurations is needed to understand this phenomenon. Both the stable structures at different dimer vacancy densities and the possible pathways for the diffusion of dimer vacancies to form the line defects are to be studied. Furthermore, the issue of why the multiple missing dimer configurations seem to be unstable, as they are not observed experimentally when the system is in thermal equilibrium after annealing, is also interesting. The objective of this paper is to investigate the formation mechanism of the dimer-vacancy line for various dimer-vacancy densities and to suggest some possible pathways to the line-defect formation on the Si(100) surface. Two line-defect configurations, namely perpendicular and parallel to the direction of the surface dimer row, are studied at two representative dimer-vacancy densities, one at 0.25 ML and the other at 0.5 ML, corresponding to the low and high concentration cases reported in Zandvliet’s experimental work. Various dimer-vacancy configurations, ranging from random to partially ordered to perfectly ordered dimer-vacancy line structures, have been investigated to study possible pathways for the dimer-vacancy diffusion toward the line-defect formation.

II. THEORETICAL APPROACH

A tight-binding (TB) total-energy scheme parametrized by Goodwin, Skinner, and Pettifor (GSP) has been adopted to study the ordering of dimer vacancies on the Si(100) surface in the present work. In the TB scheme, the total energy of the Si system is defined as

$$E_{\text{total}} = \sum_{\text{occupied}} \sum_n \langle \Psi_{I,n}|H_{\text{TB}}|\Psi_{I,n}\rangle + \sum_{I<J} \phi(|\vec{r}_I-\vec{r}_J|)$$

(1)
at zero temperature, where $\Psi_{I,n}$ is the wave function on the $I$th atom with $n$ electronic orbitals, $H_{\text{TB}}$ the tight-binding Hamiltonian, and $\phi$ the two-body repulsive potential. The force on the $I$th atom is defined as

$$\vec{F}_I = M_I \frac{d^2 \vec{r}_I}{dt^2} = -\sum_{J=1}^{N} \langle \Psi_{J,n} | \frac{\partial H_{\text{TB}}}{\partial \vec{r}_I} | \Psi_{I,n} \rangle - \sum_{j<s} \frac{\partial \phi_{I,j}}{\partial \vec{r}_I},$$

(2)

where the first term on the second line is the so-called Hellmann-Feynman force. In Goodwin $et$ $al.$'s scheme, the hopping parameters and the two-body potentials are scaled as

$$h_{\sigma}(r) = h_{\sigma}(r_0) \left( \frac{r}{r_0} \right)^2 \exp \left[ 2 \left( - \left( \frac{r}{r_c} \right)^{n_1} + \left( \frac{r}{r_c} \right)^{n_2} \right) \right],$$

(3)

and

$$\phi(r) = \phi(r_0) \left( \frac{r}{r_0} \right)^{n_2} \exp \left[ n_2 \left( - \left( \frac{r}{r_c} \right)^{n_3} + \left( \frac{r}{r_c} \right)^{n_4} \right) \right],$$

(4)

where $h_{\sigma}$ represents the interatomic hopping parameters such as $h_{s\sigma}, h_{p\sigma}, h_{pp\sigma}$, and $h_{pp\sigma}$, and $\phi(r_0) = 3.4581$ eV is the two-body potential energy at the equilibrium distance ($r_0 = 2.35$ Å). By introducing the exponential term, a better transferability has been achieved and the tails are smoothed at large distances. The details about this scheme can be found elsewhere. This scheme is known to be accurate and effective to treat electronic interactions of silicon systems, because the overlap integrals are empirically parametrized by fitting to the universal binding-energy curves generated by the first-principles calculations for various Si phases. It has been successfully applied to the studies of defects in c-Si (Ref. 14) and in a-Si (Ref. 15) as well as the single dimer vacancy in the Si(100) surface.

To study the ordering of dimer vacancies on a defective Si(100) surface, especially when the vacancy density is high, a large supercell is required to avoid superficial effects inherited by a small supercell. In the present work, we have used a (4 $\times$ 8 $\times$ 6) supercell containing 192 silicon atoms with the bottom layer saturated by 64 hydrogen atoms. The periodic boundary condition is applied to repeat the supercell in the $x$ and $y$ directions. The steepest-descent (SD) method was adopted to get the equilibrium structure of the dimer vacancies on the Si(100) surface. Only the nearest-neighbor interactions are considered with a cutoff distance of 3.2 Å. Since the SD method may not guarantee a global minimum, the simulated annealing (SA) method was also used to test the obtained equilibrium structures of the dimer-vacancy distribution.

### III. RESULTS AND DISCUSSION

In the present TB scheme both the $c(4 \times 2)$ and the $p(2 \times 2)$ Si(100) surface structures are energetically favorable. The local dimer structures, i.e., the bond lengths and bond angles, of the $c(4 \times 2)$ and the $p(2 \times 2)$ surface obtained by the SD method are almost identical and the total-energy difference is negligible within the computational accuracy. In this study we use the $p(2 \times 2)$ symmetry on the Si(100) surface, containing 16 surface dimers arranged in a (4 $\times$ 4) pat-
tion between the dimerization effect and the strain effect. At low dimer-vacancy densities, the accumulated strains are adequately relaxed when the line defects are formed perpendicular to the direction of the dimer row as shown in Fig. 1(b), whereas at high dimer-vacancy densities, the distance between vacancy line defects is too close and thus the energy gain per dimer by the strain release is not appreciable.

Based on this analysis, we conclude that the DVL$_1$ is the stable line-defect structure on the Si$_{100}$ surface at low DVL densities below 0.25 ML. Likewise, above 0.5 ML the DVL$_i$ is expected to be more favorable. We did not search for the critical density that separates these two cases, but experimental results suggest that it is about 0.3 ML. We note that another DVL$_1$ configuration shown in Fig. 2(c) is energetically less favorable than the configuration in Fig. 2(b) by 0.20 eV per dimer vacancy. In this case, the energy gain by the buckling of the dimers on the second layer plays as important a role as that of the dimerization because the configuration in Fig. 2(c) has an even lower energy when the buckling effect is ignored. The buckling of dimers on the second layer is about 0.55 Å for both Fig. 2(b) and Fig. 2(c), which is smaller than 0.76 Å on the clean surface but larger than 0.48 Å of the surface dimers at the upper terrace edge. Contrary to that in Fig. 1(b), the configuration in Fig. 2(a) gains up to 0.07 eV per dimer by rebonding of dangling bonds, although the effect is not as significant as in Fig. 2(b). This difference can be understood as the result of the anisotropy of surface stress on the Si$_{100}$ surface.

The calculated results reported above can be understood from the physical picture obtained previously for the single dimer-vacancy case, where the nonbonding model can be energy lowered by enhancing the $\pi$ bonding character. As the strain effect gets weaker, the weak bonding structure starts to appear in order to reduce the number of dangling bonds, and finally the complete rebonding structure can be achieved at the strain-free surface such as a clean Si$_{100}$ surface. This type of behavior was also observed at the stepped Si surface where there are also two types of stable structures described by the nonbonding model and the rebonding model at the step edge, and they appear alternately in the stepped surface during the growth.

These results are in good agreement with the experimental observation and recently published ab initio calculations by Tsai et al. The reported calculations show that at low dimer-vacancy concentrations, the DVL$_i$ is favored and the optimum widths of these DVL’s are two to three missing dimer rows, in agreement with the experimental STM observations. On the contrary, the DVL’s with a width greater than three missing dimer rows generally have their orientation parallel to the direction of the dimer row, which usually occurs at higher vacancy densities.

We next consider the possible pathways for the formation of the line defects on the Si$_{100}$ surface upon annealing. In previous studies of the diffusion mechanism for a single missing dimer on the Si$_{100}$ surface, it was found that a single dimer vacancy can diffuse to the most stable configuration under the circumstances through the bond-breaking mechanism and the place-exchange mechanism after overcoming a diffusion barrier of about 1.7–2.3 eV. The same analysis can also be applied to the multiple missing
dimer vacancies studied in the present work.

The issue here is to understand the underlying physics of the transition from randomly distributed multiple dimer vacancies to the ordered line-defect structures observed in experiment. We examine in detail the case of 0.25-ML dimer-vacancy coverage to illustrate the dimer-vacancy diffusion and the possible pathways toward the formation of line defects on the Si\(\text{100}\) surface. A large number of dimer-vacancy configurations ranging from random to ordered line structures have been investigated. As a representative example of the transition from a random dimer-vacancy distribution toward the stable ordered line-defect structure, Fig. 3 shows a likely pathway for dimer-vacancy diffusion starting from a square crater pattern. It should be mentioned that randomness is defined here as a significant deviation from the ordered dimer vacancy line configurations in the context of the finite simulation cell size used in the present work. Based on the study of an extensive set of dimer-vacancy configurations, we have found that the square crater configuration shown in Fig. 3(a) has the highest energy (0.33 eV per dimer vacancy above that of the DVL\(_{\|}\)) and other crater configurations with slight deviations from Fig. 3(a) also have energies appreciably higher than that of the DVL\(_{\|}\). This explains why such configurations, which are generated during the initial ion sputtering period, are not observed experimentally after annealing above the transition temperature. Other random configurations have energies lower than that of the crater pattern, but still relatively high compared with that of the DVL\(_{\|}\). The preferred dimer-vacancy line structure, i.e., the DVL\(_{\|}\) in the case of 0.25-ML coverage, is stable, although configurations with some slight deviations, such as the dogleg pattern shown in Fig. 3(c), are energetically competitive. These configurations should correspond to those imperfect, i.e., not entirely straight, dimer-vacancy lines observed experimentally.\(^{4,7,8,10}\) On the other hand, the unpreferred dimer-vacancy line structure, i.e., the DVL\(_{\|}\) in

FIG. 2. Top view of three dimer-vacancy line configurations on the \(p(2 \times 2)\) Si(100) surface, with a dimer-vacancy density of 0.5 ML. (a) Parallel to the surface dimer row with no rebonding effect in the second layer included, (b) perpendicular to the surface dimer row with all rebonding dimers in the second layer, (c) perpendicular to the surface dimer row with all rebonding dimers except at the boundary of the first and second layer. The numeric values indicate the bond length of dimers at the surface and the exposed second layer. The values in parentheses represent the asymmetry of dimers. All lengths are in units of Å.
the present case, and its close variants have relatively high energies. From these results, we obtain a clear physical picture for the redistribution of multiple dimer vacancies on the Si(100) surface. These multiple dimer-vacancy configurations, i.e., craterlike patterns, diffuse above the transition temperature through a set of intermediate random configurations toward the stable configurations, which include the preferred line-defect structure and its close variants.

The calculated results reported above provide an explanation for the experimentally observed temperature-driven structural transition on the Si(100) surface. At low temperatures, thermal energy is not sufficient to overcome the diffusion barrier for dimer vacancies and the originally formed random dimer-vacancy distribution will remain unchanged. Above a transition temperature of about $500^\circ$C, thermal energy can overcome the diffusion barrier and a dimer-vacancy redistribution will occur, leading to the preferred ordered and nearly ordered dimer-vacancy line structures as illustrated in Fig. 3. However, when the temperature is further increased, the configurational entropy will dominate the free energy of the system and drive the dimer vacancies on the surface into a random distribution. From the above analysis, it is clear that ordered dimer-vacancy structures such as the DVL’s can only exist in an intermediate temperature range, while at low- and high-temperature annealing the randomly distributed dimer vacancies are stable.

IV. SUMMARY

In this paper we have studied the ordering of dimer vacancies on the Si(100) surface using a tight-binding total-energy approach. The ordered dimer-vacancy line structures are found to be energetically favorable. However, random dimer-vacancy distributions originally formed on the Si(100) surface are stable at low temperatures due to a fairly high diffusion barrier for dimer-vacancy diffusion. Annealing above a transition temperature of about $500^\circ$C induces a random-ordered structural transition for the dimer-vacancy distribution on the Si(100) surface. At low missing dimer densities, the strain effect dominates and dimer vacancies transform into line defects perpendicular to the direction of the surface dimer rows upon annealing above the transition temperature. When the dimer-vacancy density increases, the dimerization effect becomes more important and, as a result of the competition between the strain effect and the rebonding effect, the line defects align parallel to the surface dimer row. We have calculated the energies of a large number of dimer-vacancy configurations to study possible pathways for these transformations through dimer-vacancy diffusion. The calculated results are in good agreement with experiment. The theoretical analysis presented in this work provides a physical understanding of the multiple dimer-vacancy distribution and the temperature-driven structural transition observed on the Si(100) surface.

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Dimer-vacancy configurations formed on the Si(100) surface can be quite stable unless annealed at high temperatures, since migration from one configuration to another must overcome a fairly large diffusion barrier height of about 1.7–2.3 eV. From the simple Redhead’s analysis of activation temperature [R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces* (Wiley, New York, 1996), Chap. 7], \( E_a = 0.06T \) kcal/(mol K), where \( E_a \) is the activation energy and \( T \) is the migration temperature that we have estimated to be about 380–610 °C. This value is in good agreement with the experimentally observed transition temperature of 500 to 600 °C.