RAPID COMMUNICATIONS

Dimer-vacancy–dimer-vacancy interaction on the Si(001) surface:
The nature of the $2 \times n$ structure

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An increase of dimer vacancies on the Si(001)-2×1 surface after radiation quenching from high temperatures has been observed using STM. After further quenches, vacancies nucleate into chains running perpendicular to the dimer rows. These vacancy chains then connect and develop into vacancy lines (VL's) that extend for many thousands of Å. Each VL consists of mainly two types of dimer vacancies: a divacancy and the combination of a single vacancy and a divacancy separated by an isolated dimer. All the VL's together with the dimer rows form a $2 \times n$ structure with $6 \leq n \leq 12$. Calculations using the Stillinger-Weber potential have been performed to examine the ordering mechanism of dimer vacancies.

The Si(001) surface is a widely studied surface due not only to its technological importance but also to its amazingly complex reconstructions under various conditions. For a clean Si(001) surface, besides the commonly observed 2×1 structure,[1,2] the $c(2 \times 4)$ reconstruction has also been observed at low temperatures.[3,4] In addition, the transition from single- to double-atomic-height steps on large miscut surfaces[5,6] as well as the coexistence of straight and wavy steps on very flat surfaces[7,8] has been reported. It is known that the Si(001) surface contains a certain percentage of dimer vacancies since the first scanning tunneling microscopy (STM) images were observed.[2] An *ab initio* total-energy calculation on the atomic structures of different dimer vacancies and vacancy clusters has been carried out by Wang, Arias, and Joannopoulos.[9] Through annealing and slow cooling, Swartzentruber *et al.* have demonstrated that the dimer vacancy concentration can be manipulated.[10]

First observed by Müller *et al.*,[11] the $2 \times n$ reconstruction has since been studied by a number of groups[12–20] using various surface preparation techniques. It is clear that metal contamination, especially Ni contamination, leads to the $2 \times n$ structure.[12–14] However, Martin *et al.* found little trace of Ni on the thermally quenched $2 \times n$ surface.[15] Aruga and Murata observed the coexistence of 2×1 and $2 \times n$ on the same surface but in different regions.[16] Because Ni atoms migrate easily on the Si surface at high temperatures, the coexistence of $2 \times n$ and 2×1 is unexpected if the Ni contamination is the only cause for producing the $2 \times n$ structure. The experiment of the desorption of oxide layers from the Si(001) surface performed by Johnson *et al.*[17] also showed the $2 \times n$ structure, which reverts back to the 2×1 structure after heating. After the annealing of Ar-bombarded Si(001) surfaces, Zandvliet and co-workers[18,19] reported the observation of the $2 \times n$ structure as well.

If we assume that the $2 \times n$ structure contains one nickel atom per unit cell, it would give Ni concentrations of 5% for $n = 10$ and 8% for $n = 6$. By placing a Ni strip of nm thickness on a clean Si(001) surface followed by heating and quenching, Dolbak *et al.*[21] have shown that the Ni concentration determined from Auger measurements is always less than 1% for the $2 \times n$ structure.[22] This Auger experiment as well as experiments described earlier[15–19] indicate a strong likelihood that the $2 \times n$ ordering is governed by some mechanism that does not require a Ni concentration of one Ni atom per unit cell.

In this paper we present a STM study, in conjunction with theoretical calculations using the Stillinger-Weber potential, of the $2 \times n$ structure. We conclude that the $2 \times n$ structure results from the ordering of dimer vacancies (DV's) through the DV-DV interaction. We have also identified the two main building blocks of the $2 \times n$ structure. The STM line scans made on these two types of DV's further confirm that second-layer atoms rebond in preferred manners to reduce the number of dangling bonds.

The experiment was performed with an ultrahigh vacuum chamber equipped with a homemade STM system[30] and a commercial visual low-energy electron diffraction optics. The chamber base pressure was maintained in the mid 10^{-11}-torr range. Si(001) samples with a miscut angle of 0.08° and a size of 0.15×0.6×0.02 in.^{3} were first outgassed in the heating stage at 700 °C for a few hours before heating to above 1150 °C followed by 900 °C annealing. A sample cleaned in the above manner was then transferred to the scanning tunneling microscope for observation. Such a surface displays terraces with alternating 1×2 and 2×1 dimer reconstructions. These terraces are separated by single-atomic-height steps and have an average width ~1000 Å. Care has been taken to ensure that samples have only made contact with Ta clips from the front, Mo supporting bars from the back.
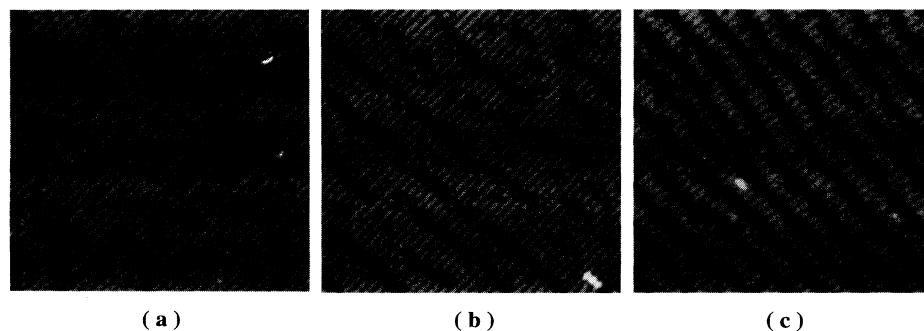
(a)   (b)   (c)

FIG. 1. STM images taken at different quenching stages showing the $2\times n$ structure. In (a), dimer vacancies start to form short vacancy chains (VC's) in the direction perpendicular to the dimer rows. In (b), the surface is covered with long VC's which are about to form uninterrupted vacancy lines (VL's). It is noted that there are not many dimer vacancies between two neighboring VC's. (c) shows the final $2\times n$ structure with VL's continuing for thousands of Å's. All images have the same size of 280×280 Å^2. In (c), $n\sim7.5$.

By continuously quenching a clean Si(001) surface from above 1000 °C, we have observed an increase in the DV concentration. The surface structure at various quenching stages is shown in Fig. 1. In Fig. 1(a), a surface with a DV concentration slightly higher than that of a well-annealed surface is shown. A few short vacancy chains can be seen in the figure. After further annealing, long vacancy chains are formed [Fig. 1(b)]. These vacancy chains run perpendicular to the dimer rows. It is interesting to point out that there are only a limited number of DV's appearing in between two vacancy chains. These vacancy chains grow in length and eventually connect and form vacancy lines (VL's) [Fig. 1(c)]. The distance between two adjacent VL's is between $6a$ and $12a$, where $a=3.84$ Å is the surface lattice constant. The VL's extend for thousands of Å without interruption. It is noted that some VL's continue right to the step edges. No DV concentration gradients have been observed on either side of the two types of steps.[23]

We have examined the surface structure along the length of the sample. There is no observable difference in terms of DV concentration at different locations. Should metal impurities play a major role in the creation of DV's, we would expect that regions closer to the two ends that make direct contact with Ta clips are affected more strongly than in the middle region. However, we are not able to rule out the possibility of having a minute amount of metal impurity on the surface. Through annealing and slow cooling cycles, we are able to break the VL's into vacancy chains but cannot totally remove these vacancy chains.

Efforts have been made to identify the basic building blocks of the VL's. We have closely examined 1000 DV sites. The two most frequently appearing DV structures have been identified as the 2-DV (a cluster of two missing dimers) and the (1+2)-DV (a combination of a single DV and a 2-DV separated by a dimer).[24] About 95% of a VL is made of 2-DV's and (1+2)-DV's with the (1+2)-DV being slightly favored. The other 5% consists of 3-DV's (clusters of three DV's), (1+2+1)-DV's (combinations of a DV, a dimer, a 2-DV, a dimer, and a DV), (1+3)-DV's (combinations of a DV, a dimer, and a 3-DV), and occasionally (2+2)-DV's (a 2-DV, a dimer, and a 2-DV).

For those straight sections within a VL, a structure of alternating 2-DV's and (1+2)-DV's is regularly observed. For sections that meander, however, no obvious DV pattern

emerges. Nor does a pattern exist for two DV's in the same dimer row but from two neighboring VL's.

In order to examine the rebonding of the second-layer atoms in a VL, line scans across the VL's in the direction parallel to the dimer rows have been examined. Typical line cuts obtained from STM images are displayed in Figs. 2(a)
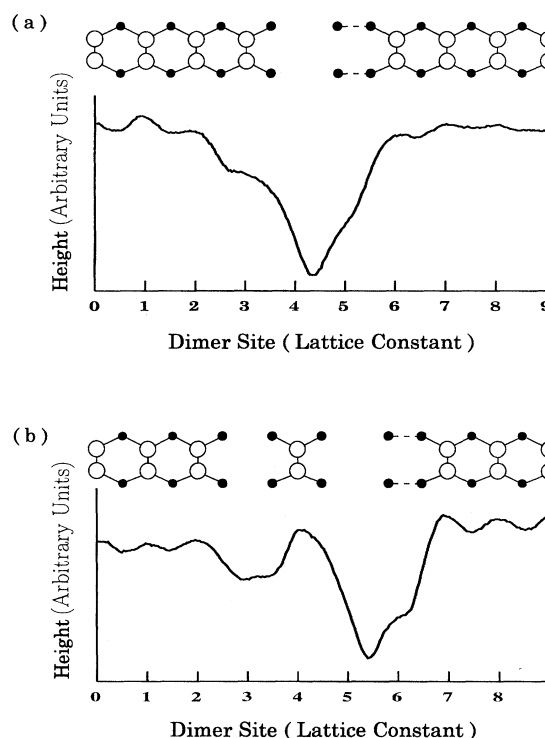

FIG. 2. Typical line scans across a VL. In (a), two distinct features are shown on both sides of the 2-DV valley: the dimer on one side shows a depression and a peak appears on the other side. In (b), a peak shows up on the side of the divacancy that is further away from the single DV. The atomic structures calculated using the Stillinger-Weber potential for the 2-DV and the (1+2)-DV are shown at the top of each line scan. The rebondings of the second-layer atoms are indicated by the dashed lines. Only atoms in the top two layers are shown. Atoms indicated by open circles are surface dimers.

and 2(b). In Fig. 2(a), a line cut for the 2-DV is shown. Two unique features are displayed: (1) a dimer is depressed on one side of the 2-DV indicating the relaxation of this dimer in response to the missing dimers and (2) a small peak shows up on the opposite side of the divacancy. In Fig. 2(b), a line cut for the (1+2)-DV is shown. A small peak is observed on the far side of the divacancy valley with respect to the single vacancy. There is no sign of dimers being depressed on either side of the divacancy.

Calculations using the Stillinger-Weber potential have been performed to examine the rebonding of the second-layer atoms for various types of vacancy configurations. In the calculation, 3250 Si atoms distributed in eight layers have been employed. Of these, $(1827-m)$ atoms in the top five layers are fully relaxed and the remaining atom are fixed in their respective bulk positions. m is the number of atoms to be removed in forming various vacancy configurations. The results are shown in Figs. 2(a) and 2(b) as top views of dimer rows containing the two elementary building blocks of a VL. In Fig. 2(a), a dimer row with a divacancy is shown above the line cut. The second-layer atom pair at the center of a 2-DV rebonds to the other atom pair on one of the two sides. By doing so, the number of dangling bonds is restored to that of a perfect 2×1 surface at the expense of increasing the strain energy, as pointed out by Pandey[25] and Tersoff.[26] In Fig. 2(b), a dimer row with a (1+2)-DV is shown. Rebonding occurs in the divacancy of the (1+2)-DV on the side further away from the single dimer vacancy. The results agree well with the respective STM line scans and with those proposed by Wang, Arias, and Joannopoulos.[9]

Stillinger-Weber-type calculations have also been performed on structures made from 2-DV's and (1+2)-DV's that mimic sections of a VL. Such calculations provide the binding energies for various DV clusters. The lowest energy configuration for two adjacent 2-DV's and for two adjacent (1+2)-DV's is shown in Figs. 3(a) and 3(b), respectively. A surface with two 2-DV's [(1+2)-DV's] separated far apart has an energy of 0.08 (0.28) eV higher than that of a surface shown in Fig. 3(a) [3(b)]. The excess energy represents an attractive interaction for the two DV's in neighboring dimer rows. This attraction is the driving force for the DV's to form VL's, which run perpendicular to the dimer rows. That the binding energies are on the order of a couple of tenths of an eV for different VL configurations agrees with the fact that, after quenching from 1000 °C, (1+2)-DV's and 2-DV's appear essentially random in a VL.

It is difficult to pinpoint the formation energies of various types of dimer vacancies because there are a number of atom sites in a step edge that the excess atoms can attach to. The structure of a step plays an important role in determining the formation energies as well. With the above-mentioned complications in mind, we have calculated the formation energy of a 2-DV. In the calculation, a large ($\sim$4000 atoms) cluster containing an S_B step has been employed (it costs more energy to create kinks on a S_A step). The large-size cluster is needed to ensure that there is not interaction between the 2-DV and either the step kink sites or the step. Under the condition that the introduction of the four excess atoms to the step edge does not change the rebonding of edge atoms, we have obtained the 2-DV formation energies of (i) 1.09 eV for the case of the excess atoms being attached to a straight
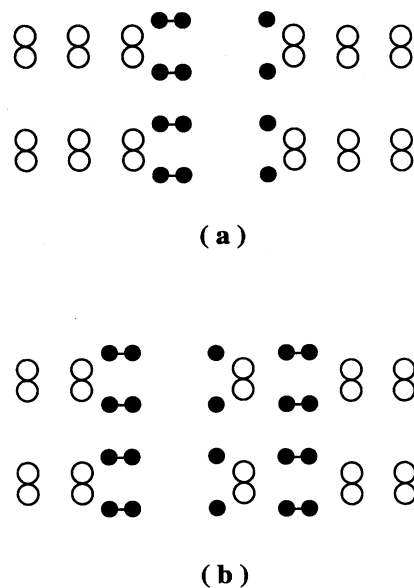

(a)

(b)

FIG. 3. Lowest energy configurations for two DV pairs. In (a) and (b) pairs of 2-DV's and (1+2)-DV's are shown, respectively. A surface with two 2-DV's [(1+2)-DV's] separated far apart has an energy of 0.08 eV (0.28 eV) higher than that shown in (a) [(b)]. The attractive interaction is short ranged. Open and filled circles are for top- and second-layer atoms, respectively. Second-layer atom rebondings are indicated. Dimer rows run in the horizontal direction.

S_B step and (ii) 0.84 eV for the case of the excess atoms being attached to a single kink site that has two consecutive missing dimers in the same dimer row so that a straight S_B step results after the kink site is annihilated by the four excess atoms.

Is the $2 \times n$ structure intrinsic to the Si(001) surface? It is our conjecture that there are a number of surface preparation procedures that are capable of creating a high DV-concentration surface. The $2 \times n$ structure does not depend on particular preparation procedures and is driven by the DV-DV interaction described earlier.

It is our experience that the DV density depends strongly on how the surface is prepared. A surface with a DV density as high as 10% can be obtained. However, after carefully annealing a surface, a DV density close to 1% can also be reached. Since the $2 \times n$ surface has a DV density of $\sim$30%, which is much higher than the 10% mentioned above, this poses an interesting question as to how the DV's in the $2 \times n$ structure are created. One of the possible mechanisms for generating high DV-density surfaces is that the DV density is temperature dependent. Such a dependence agrees with the general trend of the described observation. At high temperatures, DV's are mobile enough to move around. As the surface temperature falls into some range during the quenching process, the attractive force between the DV's in neighboring dimer rows overcomes the thermal fluctuation, and vacancy chains appear as a result of the formation of bond states. These vacancy chains survive later quenches while new DV's are constantly generated to satisfy the steady-state concentration at high temperatures.

For a clean surface, (1+2)-DV's, single DV's, and (1+3+1)-DV's are all more populous than 2-DV's.[9] However, in

the $2 \times n$ structure mainly (1+2)-DV's are observed. Since the dimerized surface is under compression along dimer rows,[27] it is likely that the (1+2)-DV and the 2-DV are favored over other types of DV's in relieving the surface compression.

Park et al.[28] and Chen et al.[29] have reported observations of the $2 \times n$ structures by growing Bi and Ge on Si(001), respectively. In these two systems, however, the VL's consist of only single DV's. It is therefore reasonable to ask why totally different systems can exhibit similar surface reconstructions and yet a major difference exists in the VL structures. For Ge/Si(001) and Bi/Si(001), the surfaces are under tension in the dimer row direction instead of compression for the clean Si(100) surface. From the viewpoint of balancing the surface stress, the differences in VL configurations probably are not too surprising since single DV's likely create stress fields more accommodating to tensile stress. The agreement on the surface atom periodicities, i.e., the $2 \times n$ structure, however, is interesting. Whether such an agreement is accidental, or due to some more subtle reasons, still remains to be explored.

In conclusion, we have observed the $2 \times n$ reconstruction that is induced by the intrinsic DV-DV interaction. At elevated temperatures, DV's are able to move around, form dimer vacancy chains, and eventually connect into VL's. The $2 \times n$ $(6 \leq n \leq 12)$ phase consists of VL's of many thousands of Å long in a direction perpendicular to the dimer rows. The basic building blocks for the VL's are mostly 2-DV's and (1+2)-DV's. Structures for second-layer-atom rebonding have been calculated and compared with observations.

Note added. We were recently informed by H. J. W. Zandvliet that he and co-workers have also observed similar VL structures on the $2 \times n$ surface.

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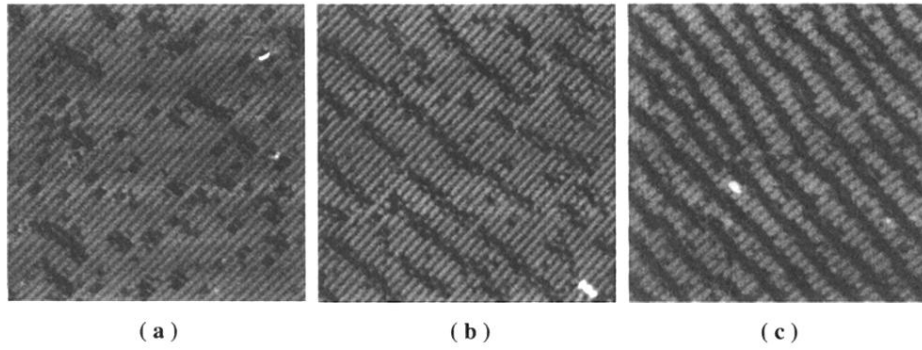[30] A. R. Smith and C. K. Shih, Rev. Sci. Instrum. **66**, 2499 (1995).

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