

Scanning tunneling microscopy investigation of the dimer vacancy–dimer vacancy interaction on the Si(001) $2 \times n$ surface

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(Received 25 July 1995; accepted 10 December 1995)

Scanning tunneling microscopy has been used to investigate the formation of the $2 \times n$ vacancy line structure on Si(001). We find that quenching the surface from high temperatures results in the formation of vacancies. After further quenching, these vacancies nucleate into chains running perpendicular to the dimer rows. Finally, the vacancy chains connect and develop into vacancy lines which extend for many thousands of Å's. Each vacancy line consists of mainly two types of dimer vacancies: (1) a di-vacancy and (2) a combination of a single vacancy and a di-vacancy separated by an isolated dimer. All the vacancy lines together with the dimer rows form a $2 \times n$ structure with $6 \leq n \leq 12$. Calculations using the Stillinger–Weber potential support the view that the formation of the vacancy line structure is due to the interaction between vacancies. © 1996 American Vacuum Society.

I. INTRODUCTION

The Si(001) surface has become one of the most widely studied surfaces in part due to technological applications, but perhaps more so due to its amazingly complex and interesting surface reconstructions. For a clean Si(001) surface, the 2×1 reconstruction is commonly observed at room temperature^{1,2} while the $c(2 \times 4)$ reconstruction has also been observed at low temperatures.^{3,4} It has also been known that this surface contains a certain percentage of dimer vacancies since the first scanning tunneling microscopy (STM) images were observed.² Surfaces with vacancies, vacancy clusters, and different vacancy concentrations have been studied both theoretically and experimentally by a number of authors.^{5,6} Yet perhaps the most interesting surface reconstruction occurs at sufficiently high vacancy concentrations such that the vacancies are found to arrange into regularly spaced vacancy lines, resulting in the Si(001) $2 \times n$ reconstruction.

First observed by Müller *et al.*,⁷ the $2 \times n$ reconstruction has since been studied by a number of groups^{8–16} using various surface preparation techniques. An obvious issue which springs to mind is what is the underlying mechanism for this reconstruction. While it is clear that metal contamination, especially Ni contamination, leads to the $2 \times n$ structure,^{8–10} this fact has led to the widely accepted view that the $2 \times n$ structure is direct evidence for Ni contamination and that Ni atoms may in fact lie directly beneath the vacancy lines. However, Martin *et al.* found little trace of Ni on the thermally quenched $2 \times n$ surface.¹¹ Aruga and Murata observed

the coexistence of 2×1 and $2 \times n$ reconstructions on the same surface but in different regions.¹² Yet since Ni atoms migrate easily on the Si surface at high temperatures, this observation is unexpected if Ni contamination is the only cause of the $2 \times n$ structure. Furthermore, Johnson *et al.* desorbed oxide layers from the Si(001) surface¹³ which resulted in the $2 \times n$ structure, but the surface reverted back to the 2×1 structure after heating. Finally, after annealing Ar bombarded Si(001) surfaces, Zandvliet *et al.*^{14,15} reported the observation of the $2 \times n$ structure as well. All of these observations suggest that Ni is not the sole cause of the $2 \times n$ reconstruction.

How many nickel atoms would be necessary to account for the $2 \times n$ reconstruction? If we assume that the $2 \times n$ structure contained one nickel atom per unit cell, this would give Ni concentrations of 5% for $n=10$ and 8% for $n=6$. Yet by placing a Ni strip of nm thickness on a clean Si(001) surface followed by heating and quenching, Dolbak *et al.*¹⁷ showed that the Ni concentration determined from Auger measurements is always less than 1% for the $2 \times n$ structure.¹⁸ This experiment as well as those described earlier^{11–15} indicate a strong likelihood that the $2 \times n$ ordering is governed by mechanisms which certainly do not require a Ni concentration of one Ni atom per unit cell.

The authors of this article acknowledge the fact that Ni can lead to the $2 \times n$ structure. The specific role which Ni or other metal contaminants may play, however, is unclear. Here we present an STM study of the $2 \times n$ structure together with theoretical calculations based on the Stillinger–Weber potential. The results of this study provide strong evidence for a mechanism responsible for the ordering of the dimer vacancies (DV), namely the DV–DV interaction. We further identify the two primary DV building blocks of the $2 \times n$

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structure. In addition, STM line profiles across these two types of DV's confirm that second-layer atoms rebond in preferred manners to reduce the number of dangling bonds.

II. EXPERIMENTAL DETAILS

The experiment was performed in an ultrahigh vacuum (UHV) chamber equipped with a homemade STM system²⁵ and commercial visual low-energy electron diffraction (LEED) optics. The chamber has a base pressure in the mid 10^{-11} Torr range. STM tips are electrochemically etched tungsten wires which are further treated in the vacuum chamber by electron bombardment. Si(001) samples with miscut angles of 0.08° and a size of 0.15 in. \times 0.6 in. \times 0.02 in. are first outgassed in the heating stage at 700°C for a few hours before heating to above 1150°C followed by 900°C annealing. Samples cleaned in this manner result in STM images showing 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 the samples only contact Ta clips from the front and Mo bars from the back. After repeatedly quenching a clean Si(001) surface from above 1000°C down to near room temperature, we have observed an increase in the DV concentration.

III. EXPERIMENTAL RESULTS

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 Fig. 1. After further quenching, longer vacancy chains are formed as shown in Fig. 1(b). These vacancy chains run perpendicular to the dimer rows. One may note that there are only a limited number of DVs appearing between the vacancy chains. After even more quenching, these vacancy chains grow in length and eventually connect to form vacancy lines (VLs), as shown in Fig. 1(c). The distance between two adjacent VLs is between $6a$ and $12a$, where $a=3.84$ Å, the surface lattice constant. The VLs extend for thousands of Å's without interruption, often continuing right up to the step edges. No DV concentration gradients have been observed on either side of the two types of steps.¹⁹

Next consider the STM image shown in Fig. 2 which is an example of a $2\times n$ "island" which somehow survived the final quenching process to be left totally isolated in the middle of another large $2\times n$ terrace. The dimensions of this small island are approximately 200 Å \times 50 Å. Five clear segments of the $2\times n$ structure remain intact. Additionally, the S_A sides of the island are perfectly straight. Finally, it is interesting that such a small island of $2\times n$ exists.

We have furthermore examined the surface structure along the length of the sample. We find no observable difference in terms of the DV concentration at different locations. Should metal impurities play a major role in the creation of DVs, we would expect that regions closer to the two ends which make direct contact with the Ta clips would be affected more strongly than regions toward the middle of the

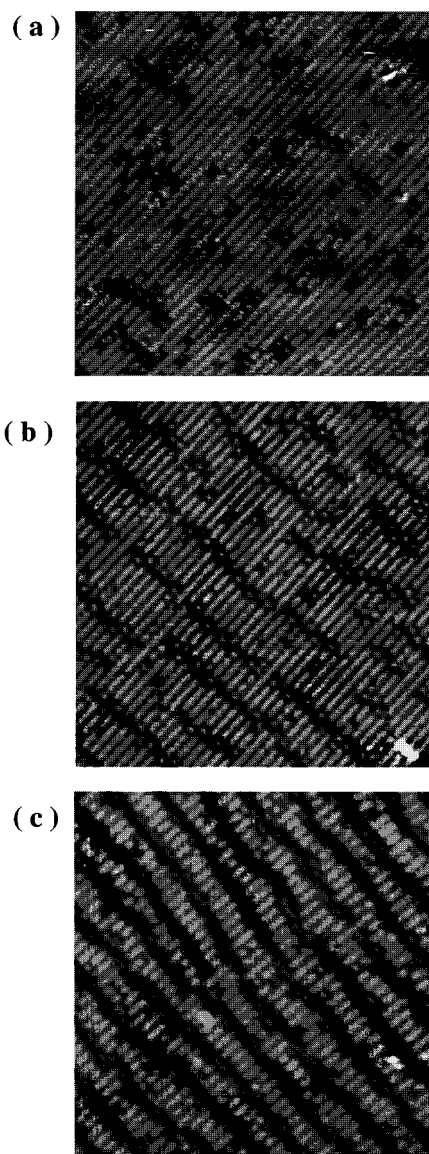


FIG. 1. STM images taken at different quenching stages showing the $2\times n$ structure. (a) Dimer vacancies start to form short vacancy chains (VC) in the direction perpendicular to the dimer rows. (b) Surface is covered with long VCs which are about to form uninterrupted vacancy lines (VLs). It is noted that there are not many dimer vacancies between two neighboring VCs. (c) Final $2\times n$ structure with VLs continuing for thousands of Å's. All images have the same size of 280 Å \times 280 Å. (c) $n\sim 7.5$.

sample. 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, however, we are able to break the VLs into vacancy chains but cannot totally remove these vacancy chains.

We now discuss the identification of the basic building blocks of the VLs. We have closely examined over 1000 DV sites. The two most frequently appearing DV structures have been identified as (1) a 2-DV (two adjacent missing dimers) and (2) a 1+2-DV (a single missing dimer and a 2-DV separated by a dimer).²⁰ About 95% of a given VL is made up of these two types with the 1+2-DV being slightly favored. The

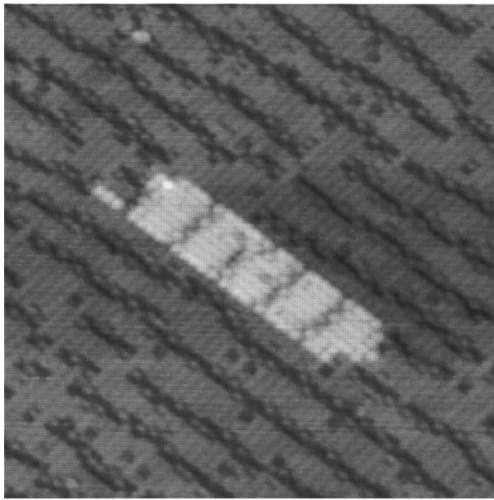


FIG. 2. 350 Å×350 Å STM image acquired at a sample bias of −2.48 V and a tunneling current of 0.65 nA showing the existence of a $2 \times n$ island on top of a larger $2 \times n$ terrace.

other 5% of the total consists of 3-DVs (three adjacent missing dimers), 1+2+1-DVs (one missing dimer+one dimer+two missing dimers+one dimer+one missing dimer), 1+3-DVs (one missing dimer+one dimer+three missing dimers), and occasionally 2+2-DVs (two missing dimers+one dimer+two missing dimers).

We have also examined the VLs to see if there exist any interesting or possibly repeated patterns of DV types. For straight sections within a VL, a structure of alternating 2-DVs and 1+2-DVs is commonly observed. For VL sections that meander, however, no obvious DV pattern emerges. Nor do we find any pattern for DVs within the same dimer row but in adjacent VLs.

In order to examine the rebonding of the second-layer atoms in a VL, line profiles across the VLs in the direction parallel to the dimer rows have been examined. Typical profiles obtained from STM images are displayed in Figs. 3(a) and 3(b). In Fig. 3(a), a profile across a 2-DV is shown. Two unique features should be pointed out: (1) a dimer is depressed on one side of the 2-DV, indicating the relaxation of this dimer in response to the two missing dimers; and (2) a small peak shows up on the opposite side of the di-vacancy. In Fig. 3(b), a profile across a 1+2-DV is shown. A small peak is observed on the far side of the di-vacancy valley with respect to the single vacancy, but there is no sign of dimers being depressed on either side of the di-vacancy.

IV. THEORETICAL RESULTS

Theoretical calculations using the Stillinger–Weber potential have been performed to investigate the rebonding of the second-layer atoms for various types of vacancy configurations. In the calculation, 3250 Si atoms distributed in eight layers were employed. Of these, $(1827 - m)$ atoms in the top five layers are fully relaxed and the remaining atoms are fixed in their respective bulk positions (m is the number of atoms to be removed in forming various vacancy configura-

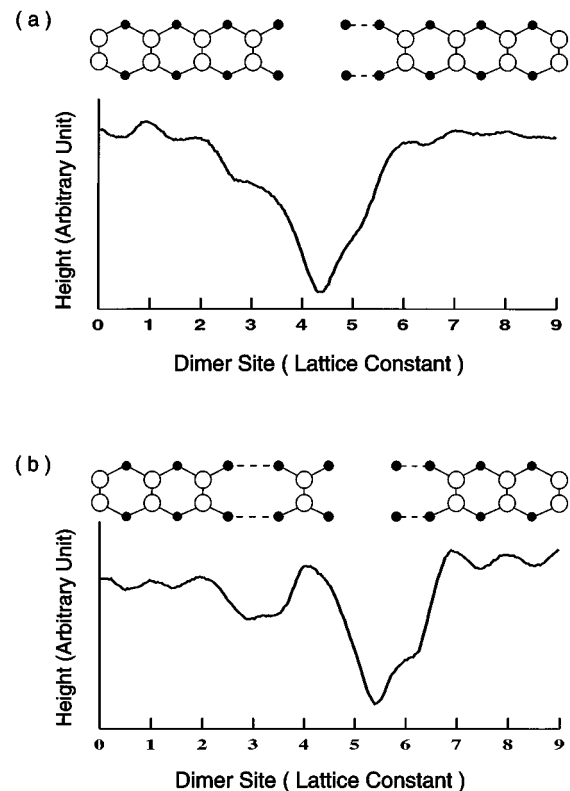


FIG. 3. Typical line scans across a VL. (a) Two distinct features are shown on both sides of the 2-DV valley: the dimer on one side shows a depression and a peak appears on the other side. (b) A peak shows up on the side of the di-vacancy which is further away from the single DV. Atomic structures calculated using the Stillinger–Weber potential for the 2-DV and the 1+2-DV are shown at the top of each line scan. 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.

tions). The results of the calculations are shown in Figs. 3(a) and 3(b) for direct comparison with the experimental data. In Fig. 3(a), the second-layer atom pair at the center of a 2-DV rebonds to the atom pair on one side. By doing so, the number of dangling bonds is restored to that of a perfect 2×1 surface but at the expense of increasing the strain energy, as pointed out by Pandey²¹ and Tersoff.²² Similarly, in Fig. 3(b) second-layer atom rebonding occurs within the di-vacancy of the 1+2-DV on the side furthest away from the single dimer vacancy, in good agreement with the STM line profile.

Stillinger–Weber-type calculations have also been performed on structures made from 2-DVs and 1+2-DVs which mimic sections of a VL in order to calculate the binding energies for various DV configurations. The lowest energy configurations for two adjacent 2-DVs and for two adjacent 1+2-DVs are shown in Figs. 4(a) and 4(b), respectively. A surface with two 2-DVs (1+2-DVs) separated far apart has an energy of 0.08 (0.28) eV higher than that of a surface corresponding to the model shown in Figs. 3(a) and 3(b). The excess energy represents an attractive interaction for the two DVs in neighboring dimer rows. This attraction is the driving force for the DVs to form VLs which run perpendicular to the dimer rows. That the binding energies are on the order of

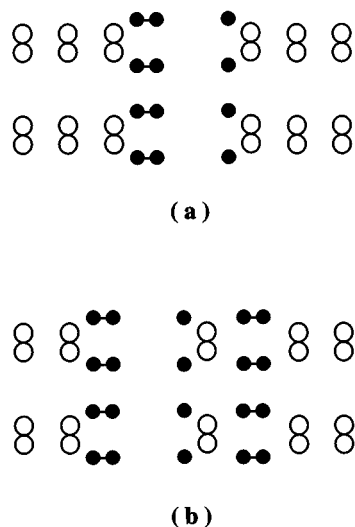


FIG. 4. Lowest energy configurations for two DV pairs. (a) and (b) Pairs of 2-DVs and 1+2-DVs are shown, respectively. A surface with two 2-DVs (1+2-DVs) separated far apart has an energy of 0.08 eV (0.28 eV) higher than that shown in (a). (b) Attractive interaction is short ranged. Open and filled circles are for top- and second-layer atoms, respectively. Second-layer atom rebondings are indicated. Dimer rows run in the horizontal direction.

a couple of tenths of an eV for different VL configurations agrees with the fact that, after quenching from 1000 °C, 1+2-DVs and 2-DVs appear essentially random within a VL.

V. DISCUSSION

What is responsible for the formation of the DVs? 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 normally be obtained. Yet, after careful annealing of the surface, the DV density can be reduced to near 1%. But the $2 \times n$ structure contains around 30% DVs. One possible explanation for high DV-density surfaces is that the DV density is temperature dependent. At high temperatures, DVs are mobile enough to move around. As the surface temperature falls into some lower range during the quenching process, the attractive force between the DVs 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 DVs are constantly generated to satisfy the steady-state concentration at high temperatures.

One may also ask the question “is the $2 \times n$ structure intrinsic to the Si(001) surface?” Park *et al.*²³ and Chen *et al.*²⁴ have reported observations of the $2 \times n$ structures by growing Bi and Ge on Si(001), respectively. In these two systems, however, the VLs consist of only single DVs. However, in the $2 \times n$ structure mainly 1+2-DVs and 2-DVs are observed, as previously discussed. A possible explanation for these differences is that in the cases of Ge/Si(001) and Bi/Si(001), the surfaces are under tension in the dimer row direction. Single DVs are likely more accommodating to the

tensile stress. On the other hand, the normal Si(001) 2×1 surface is under compression along the dimer row direction. Thus, it is likely that 1+2-DV and 2-DV structures are more favorable for relieving the compressive stress. It is interesting, however, that each of these systems exhibits the $2 \times n$ reconstruction. Whether such an agreement is accidental, or due to some more subtle reasons, still remains to be explored.

VI. CONCLUSION

We have performed an STM investigation of the Si(001) $2 \times n$ structure and combined that with theoretical calculations based on a Stillinger–Weber potential. We suggest that at elevated temperatures, DVs move around, form dimer vacancy chains, and eventually connect into VLs. This ultimately results in the formation of the $2 \times n$ ($6 \leq n \leq 12$) structure consisting of VLs many thousands of Å's long in a direction perpendicular to the dimer rows. We conclude that the mechanism behind the formation of the $2 \times n$ structure is the interaction between basically two types of dimer vacancy clusters which we have identified as the basic building blocks of the $2 \times n$ structure. These are the 2-DV and the 1+2-DV. The interaction energies between combinations of these two types of DVs have been calculated and favor the formation of extended vacancy lines. In addition, structures for second-layer atom rebonding have been calculated and compare favorably with the STM observations.

ACKNOWLEDGMENTS

This work was partly supported by the National Science Foundation (Grant No. DMR-94-02938). Z. Z. was partially supported by the NSF, MRG (Grant No. DMR-91-21074), and by the DOE under contract with Martin Marietta System, Inc. (Contract No. DE-AC05-84OR21400). F. K. M. would like to thank Professor M. B. Webb for many useful discussions and suggestions. Si samples used in this study were provided by Dr. P. Wagner of Wacker Chemitronic, Burghausen, Germany.

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