

## Origin, Cause, and Electronic Structure of the Symmetric Dimers of Si(100) at 80 K

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The characteristics of the apparent symmetric dimers observed in the scanning tunneling microscope (STM) images at low temperatures (20K–200K), far below the symmetric  $\leftrightarrow$  buckled phase transition temperature, were investigated by utilizing the technique applied to fabricate an almost defect free Si(100) surface, the art of atomic manipulation, and current imaging tunneling spectroscopy. We show that the symmetric dimers are observed at metastable regions caused by the surrounding defects, and they appear symmetric as a result of flip-flop motions of buckled dimers.

KEYWORDS: scanning tunneling microscope, scanning tunneling spectroscopy, Si(100), dimer, defect

### 1. Introduction

Even though the Si(100)dimer is one of the most simple surface reconstructions, it has turned out to be a source of ever lasting controversy. A great deal of research has been devoted to elucidate its atomic configuration, optical properties, and electronic structure. In particular, scanning tunneling microscope (STM) have considerably contributed to enlighten our understandings.<sup>1–17)</sup> At room temperature, most of the dimers of Si(100) appear in a symmetric configuration in the STM images.<sup>1)</sup> The observed apparent symmetric dimers in the STM images were first considered to support the concept of symmetric dimers. However, many experimental<sup>2)</sup> and theoretical<sup>3)</sup> studies revealed the buckled dimers to be more stable than the symmetric dimers, and at present, it is believed that the buckled configuration is the ground state of the dimers. Indeed, below 200 K, Wolkow showed that most of the dimers are observed in a buckled configuration in the STM images.<sup>2)</sup> In order to understand the apparent symmetric dimers observed in the STM images at room temperature within the framework of buckled dimers, the concept of flip-flop motion was introduced. It is implied that the buckled dimers flip-flop much faster than the scanning rate of STM at room temperature, providing apparent symmetric dimers in the STM images, while the flip-flop motion is frozen at low temperatures (below 200 K), hence the dimers appear buckled.

However, even at temperatures (*e.g.*, 80 K) far below the phase transition temperature of the symmetric  $\leftrightarrow$  buckled dimers (200 K), not all of the dimers are observed in a buckled configuration. STM images published so far (in the range of 20–200 K) always show a certain ratio of dimers appearing in a symmetric configuration. What makes the situation more complicated is the report of the reappearance of the symmetric dimers at temperatures below 20 K.<sup>4)</sup> Concerning the symmetric dimers observed at low temperatures far below the symmetric  $\leftrightarrow$  buckled phase transition temperature (hereafter, low temperature indicates the range of 20 K–200 K), there are several issues which remain to be elucidated. (1) Are the symmetric dimers observed at room temperature, the same as the symmetric dimers observed at low temperatures? (2) What is the origin of the symmetric dimers observed at low temperatures; are they intrinsic or induced by external factors? (2) What is the electronic structure of the symmet-

ric dimers, is it different from the electronic structure of the buckled dimers?

In this article we address these issues by utilizing the technique to fabricate an almost defect free Si(100) surface, the art of atomic manipulation, and current imaging tunneling spectroscopy (CITS). We show that the symmetric dimers observed at low temperatures are metastable states of the surface caused by the defects on the surface. Note that we exclude symmetric dimers observed below 20 K in this article because they might have a completely different origin.<sup>4)</sup> We show that the effect of a single defect extends over a long range. Scanning tunneling spectroscopy (STS) measurements show that the electronic structure of the symmetric dimers resembles the average electronic structure of the upper and lower atoms of the buckled dimer. From these results, we conclude that the low temperature symmetric dimers appear as a result of flip-flop motions of buckled dimers, and are identical to the symmetric dimers observed at room temperature.

### 2. Experimental

N-type Si samples phosphorus-doped with a conductivity of  $0.1 \Omega\text{-cm}$  were used. The base pressure of the vacuum chamber was  $3 \times 10^{-9}$  Pa. After ultrasonic cleaning for 10 min in acetone, the Si(001) sample was loaded into the vacuum chamber and prebaked at  $\sim 600^\circ\text{C}$  for 12 h with a vacuum pressure below  $-1.0 \times 10^{-7}$  Pa. After prebaking, the sample was once flashed to  $1200^\circ\text{C}$  for 30 s to remove the oxidized layers. After the sample and sample holder are completely cooled, an additional flashing was carried out at  $1200^\circ\text{C}$  for a very short time ( $\sim 5$  s) to reduce the density of defects.

### 3. Results and Discussion

A typical STM image of the clean Si(100) surface at 80 K is shown in Fig. 1 to demonstrate the coexistence of the symmetric and buckled dimers. In this and the following figures, the symmetric dimers are colored dark. In the middle region, the dimers appear in a symmetric configuration, while in the upper-left and lower-right regions the dimer rows appear as zigzagged chains. The zigzagged chains reflect the antiferromagnetic alignment of the buckled dimers, since only the upper or lower atom of the dimer is observed by STM depending on whether the filled or empty state is probed (STM images shown in this article are those of the empty states). This ordering provides a surface reconstruction of  $c(4 \times 2)$ . Frequently, at the boundary of the buckled-symmetric dimer domains, defects are observed, as shown in a typical example

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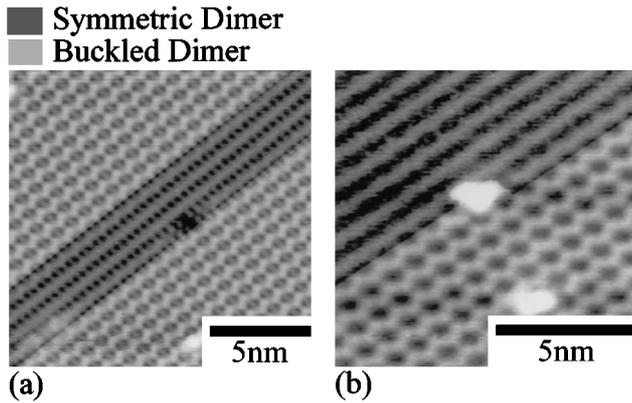


Fig. 1. (a) STM image of the clean Si(100) surface at 80 K showing the coexistence of the symmetric dimer and buckled dimer domains. The symmetric dimers are colored dark.  $V_s = +0.6$  V,  $I_t = 1$  nA. (b) A C defect at the boundary of a symmetric and buckled dimer domain.

in Fig. 1(b). Various STM studies have shown that the defects on the Si(100) surface significantly influence the configuration of the surrounding dimers.<sup>5-14</sup> For example, at 200 K, Yokoyama and Takayanagi have shown that the A defects<sup>5</sup> serve as growth nuclei of buckled dimer domains. Also, Tochiara *et al.* have shown that the C defects act as phase shifters in a complete set of buckled dimers.<sup>6</sup> Frequently, the C defects are observed at the boundaries of buckled and symmetric dimer domains.<sup>2,6</sup> Taking into consideration these results, it might be supposed that the boundaries, shapes, and size of the symmetric and buckled domains are regulated by the defects.

In order to investigate the influence of the defects, we observed the distribution of the symmetric and buckled dimer domains on various surfaces with different defect densities as shown in a set of STM images in Fig. 2. On a surface with high defect densities, the surface consists of a random mixture of symmetric and buckled dimer rows (Fig. 2(a)). As the defect density decreases, symmetric and buckled dimer domains emerge and grow in size (Figs. 2(b) and 2(c)). On the surface with a rather low defect density, the surface is covered with large symmetric and buckled dimer domains (Fig. 2(d)). This result demonstrates that the defect density is the main factor that determines the configuration of dimers at low temperatures. However, the following issues remains to be addressed, “would these symmetric domains be observed on a defect free surface?”

Recent progress in the fabrication methodology of Si(100) clean surfaces makes it possible to fabricate an almost defect-free Si(100) surface.<sup>15</sup> An STM image of a clean Si(100) surface with extremely low defect density ( $\sim 0.1\%$ ) at 80 K is shown in Figs. 2(e) and 2(f). Almost no symmetric dimers were observed, and the surface is covered with large buckled dimer domains. These experimental results suggest that the symmetric dimers observed at low temperatures are metastable regions induced by the surface defects.

The influence of individual defects (C defects) can be investigated by a unique method.<sup>16</sup> When the STM tip is positioned above a pre-selected C defect and a controlled electric field is applied by a regulated ramped bias, the C defect can be demolished. In many cases, accompanying the destruction of the C defect, an avalanche type dynamical symmetric  $\leftrightarrow$  buckled transformation of the configuration of the surround-

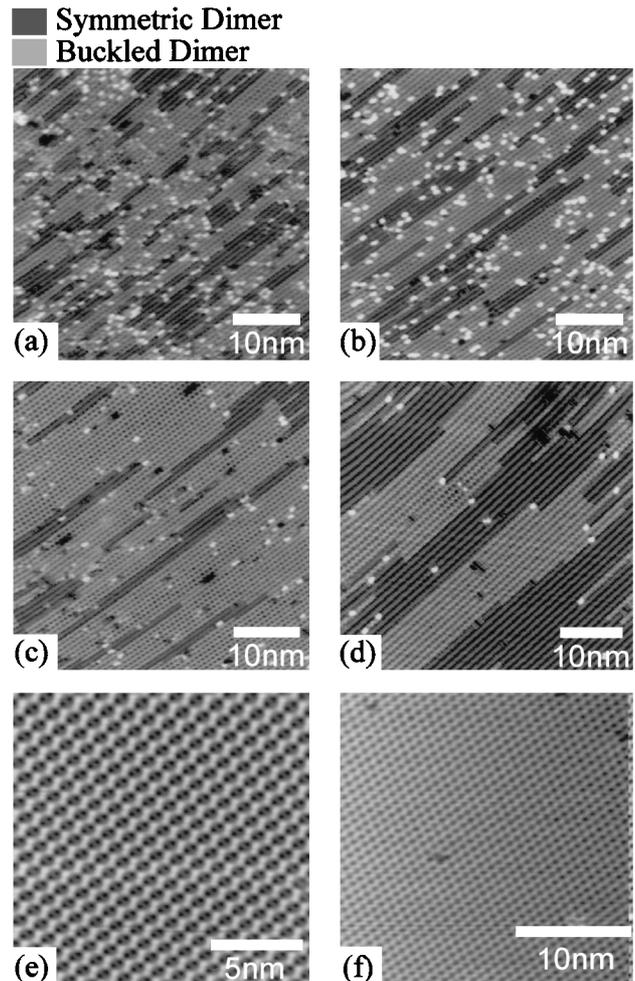


Fig. 2. (a)-(d) A set of STM images showing the influence of defects on the configuration of the surrounding dimers. The defect density decreases from (a) to (d).  $V_s = +1.0$  V,  $I_t = 1.0$  nA. The symmetric dimers are colored dark. (e), (f) STM images of a clean Si(100) surface with extremely low defect density. Temperature = 80 K.  $V_s = +0.6$  V,  $I_t = 1.0$  nA.

ing dimers was observed. Two examples are shown in the set of STM images in Fig. 3. For the case displayed in Figs. 3(1-a) to 3(1-d), we destroyed the four C defects enclosed by the white circles one after another in the order indicated by the figures written next to the circles. Accompanying each destruction, a symmetric  $\leftrightarrow$  buckled transformation of the configuration of the surrounding dimers was observed. For example, accompanying the destruction of the C defect number 1, the symmetric dimer domain observed in the initial state in Fig. 3(1-a), diminished in size and changed its shape as shown in Fig. 3(1-b). An illustrative symmetric  $\leftrightarrow$  buckled transformation was observed after destruction of the C defect numbered 4. In this case, a new symmetric dimer domain emerged after the destruction in the lower-right region as shown in Fig. 3(1-d), which was initially a single buckled dimer domain as shown in Fig. 3(1-c). It should be noted that the configuration of the dimers in between the destroyed C defect number 4 and the newly emerged symmetric dimer domain did not change but remained in a buckled configuration as can be seen from Figs. 3(1-c) and 3(1-d). This result shows that the influence of a single defect on the configuration of the surrounding dimers extends to a long distance. Figures 3(2-a) and 3(2-b) show another example. In this case, we destroyed seven C defects enclosed with the cir-

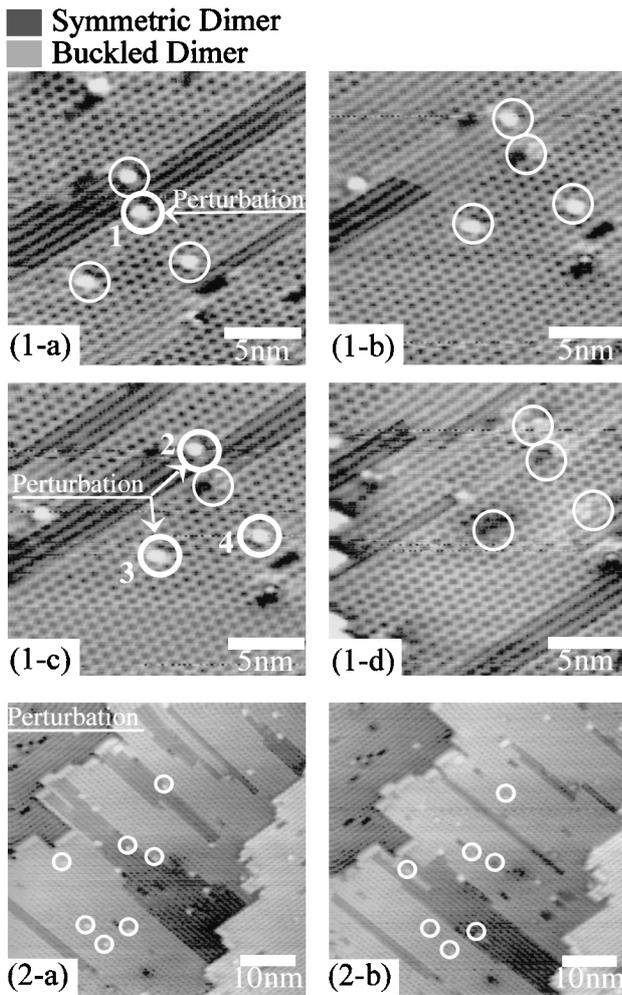


Fig. 3. (1-a) to (1-d) Four C defects enclosed by white circles were perturbed and destroyed in an order indicated by the figures. (1-a) The initial state before destruction. (1-b) After destruction 1. (1-c) Before destruction 2, 3, and 4 (1-d) After destruction 2, 3 and 4. (2-a) Initial state before destruction. (2-b) After destruction of the seven C defects enclosed by the circles.  $V_s = +0.6$  V.  $I_t = 1.0$  nA. Temperature = 80 K.

cles. Fig. 3(2-a) shows the initial state of the surface, and Fig. 3(2-b) shows the final state of the surface after all destructions were executed. By comparing the location, size, and shape of the symmetric dimer domains observed in the upper-right region of Figs. 3(2-a) and 3(2-b), it is easy to see that the influence of the destruction has extended to a couple of ten nanometers,

The surface morphologies before and after destruction can be regarded as representing the equilibrium surface configuration with and without the C defect. Therefore, comparing the configurations before and after destruction will give a unique opportunity to study the influence of the C defects on the configuration of the surrounding dimers. The drastic long range transformation of the configuration of the surrounding dimers means that the influence of individual defects extends to a long range. From these experimental results, we conclude that the low-temperature symmetric dimers emerge in metastable regions caused by the surrounding defects.<sup>13,14)</sup>

As the symmetric dimers are caused by external factors, they might have a different structure from those observed at room temperature. In fact, a real symmetric dimer is predicted to have a metallic characteristic<sup>3)</sup> while the buckled dimers

have a semiconductive feature due to charge transfer from the lower atom to the upper atom. In order to clarify this point, we carried out a CITS measurement of the symmetric and buckled dimers to resolve the electronic structure of the symmetric dimers observed at low temperatures, and to compare it with that of the buckled dimers. The normalized tunneling conductivities (STS spectra,  $(dI/dV)/(I/V)$  versus  $V$ ) are numerically calculated from the tunneling I-V spectra (not shown) extracted from the CITS data. I-V spectra show that the buckled and symmetric dimers both have a similar semiconductive feature with a surface band gap of  $\sim 0.5$  V, similar to that of the symmetric dimers at room temperature. The Fermi level is at the edge of the conduction band because the sample is n-type doped. Figure 4 shows the STS spectra of the upper and lower atom of the buckled dimer with the STS spectra taken on both sides of a symmetric dimer. The shaded region represents the energy window of the surface band gap where the tunneling noise is emphasized. Immediately it is clear that the buckled dimers and the symmetric dimers have very similar electronic structures. The similarity between the STS spectrum of the buckled dimer at low temperature and that of the dimers obtained at room temperature by Hamers. *et al.*,<sup>1)</sup> ensures that obtained STS spectra are not devalued by any possible electronic structure of the tunneling tip. The main peaks in the filled and empty states are attributed to the  $\pi$  and  $\pi^*$  surface states of the dangling bonds of the buckled dimers, respectively. The upper atom of the buckled dimer has a stronger intensity at the  $\pi$  surface state than the lower atom, while the lower atom has a stronger intensity at the  $\pi^*$  surface state than the upper atom. This result confirms the charge transfer from the lower atom to the upper atom (charge transfer from the  $\pi^*$  to  $\pi$  surface state) that was predicted by theoretical calculations and the general law of chemical bonding.

As mentioned above, theoretical calculations predict a real symmetric dimer to have a metallic feature,<sup>3)</sup> quite different from the measured semiconductive feature. Hence, we conclude that the apparent symmetric dimers observed by STM are not truly symmetric but buckled. Generally, the electronic structure of the symmetric dimer can be considered to

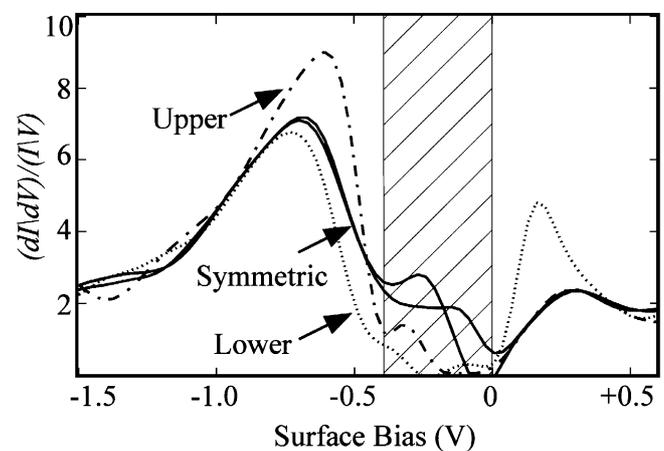


Fig. 4. STS spectra of the lower (dashed line) and upper (dashed-dotted line) atoms of the buckled dimer with two STS spectra (real lines) taken from both sides of the symmetric dimer. All of the data was taken with the same tip apex. The shaded region represents the energy window of the surface band gap where the tunneling noise is emphasized. Temperature = 80 K.

be close to the average electronic structure of the upper and lower atoms of a buckled dimer. This result strongly indicates that the apparent symmetric dimers observed at low temperatures are also caused by flip-flop motions of buckled dimers, identical to the case at room temperature.

#### 4. Conclusion

We have investigated the characteristics of the apparent symmetric dimers observed in STM images at low temperatures (20 K–200 K) far below the symmetric  $\leftrightarrow$  buckled phase transition temperature. We conclude that the cause of the symmetric dimers at low temperatures is the defects on the surface. Experimental results suggest that the symmetric dimers emerge in metastable regions caused by the surrounding defects. STS measurements show that the electronic structure of the symmetric dimers resembles the average electronic structure of the upper and lower atoms of the buckled dimer. This suggests that symmetric dimers observed at low temperatures are not really symmetric dimers but appear to be so as a result of flip-flop motions of buckled dimers, and are identical to the symmetric dimers observed at room temperature.

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