Spatially anisotropic atom extraction around defects on Si(001) using a STM

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A scanning tunneling microscope has been used to extract atoms that are adjacent to native defects on the Si(001) surface. We found a spatially anisotropic extraction frequency for the different sites around a so-called C defect. The most common occurrence is the extraction of Si atoms from a C defect to form a double dimer vacancy. Extraction of double dimers from the neighboring dimer row on one side of the defect was also observed, but dimers in the neighboring dimer row on the other side of the defect and dimers adjacent to the defect in the same row were rarely extracted. In the case of native dimer vacancy defects, few neighboring Si atoms were found to be extracted. We discuss the relationship of these observations to the energetics of defects on the Si(001) surface.

Since the low-energy-electron-diffraction (LEED) studies by Schlier and Farnsworth,[1] the structure determination of the Si(001) surface has been an object of intensive experimental and theoretical study.[2] Occupied-state STM images by Tromp, Hamers, and Demuth[3] have clearly revealed that the Si(001)2×1 surface consists of rows of oblong symmetric protrusions, consistent with the dimer model for the reconstructed Si(001) surface. Scanning-tunneling-microscope (STM) images also revealed an interesting detail that some of the dimers were obviously buckled and it appeared that the buckling of dimers was strongly associated with defects. This was an important contribution to the long-standing debate concerning the preferred dimer configuration; symmetric (flat) versus asymmetric (buckled).[4–13]

The observation of buckled dimers in the vicinity of defects naturally drew attention to the nature of the defects themselves, since they strongly influence the stable dimer configuration. Recent tunneling microscopy/spectroscopy measurements[14–16] revealed that one type of characteristic defect called the C defect on the Si(001) surface plays an important role in the physical and chemical properties of this surface. Hamers and Köhler[14] have made a careful spectroscopic measurement of the spatial extent of the defect state wave functions to clarify the geometry and electronic properties of the C defect. However, the strong voltage dependence of the STM images makes it difficult to establish the ultimate geometry of the C defect with the aid of STM images alone.

In this paper, we apply a field-induced atom-by-atom extraction technique using a STM to obtain information about the local energetics around defects on the Si(001) surface. We show how the probability of STM-induced extraction of atoms around defects is anisotropic, and discuss these results in terms of the influence of defects on the energetic stability of neighboring atoms.

The experimental procedure is similar to that described previously.[17] The samples were cut from a highly Sb-doped (n-type, $\sigma=0.01\ \Omega\,\mathrm{cm}$) commercial Si wafer. Sample cleaning in ultrahigh vacuum ($p\leq5\times10^{-10}$ Torr) was carried out by a series of flash heatings up to 1150 °C after 5 h preannealing at 800 °C and finally cooling over a period of 40–50 min to room temperature. With this method of sample cleaning, a clean 2×1 surface with an average defect density of about 5% was obtained. The pressure in the vacuum chamber was typically 5×10^{-11} Torr or lower.

To extract Si atoms from the surface, the voltage applied to the sample was ramped up to a predetermined value and the tip of the microscope was then scanned across the surface at 5 nm/s. Throughout the present experiment, the magnitude of the sample voltage during the atom extraction was fixed to -2.85 V, since this value corresponds to the condition we have determined previously[17] for extracting atoms predominantly from defect sites on the terrace. For voltages of magnitude greater than -3 V, extraction from defect-free sites also becomes common. Further, the feedback system was always active to keep the constant tunneling current of 0.45 nA irrespective of imaging mode or extraction mode.

Defects on the Si(001) surface are broadly categorized into two groups, those which induce buckling and those which do not. Figure 1(a) shows an occupied-state STM image of the Si(001) surface. Defects which induce buckling are asymmetric in appearance and are called C defects, while defects which do not induce buckling simply appear as symmetric depressions, which we call dimer vacancy defects. Examples of a C defect and a dimer vacancy defect are indicated at 1 and 2 in Fig. 1(a). As can be seen in Fig. 1(a) C defects are the most commonly observed defects on the Si(001) surface. An occupied-state STM image of smaller area containing several C defects is shown in Fig. 1(b). According to Hamers and Köhler,[14] the most probable atomic structure of the C defect is two adjacent dimers strongly buckled in the same direction, involving atomic rearrangement or a vacancy in lower

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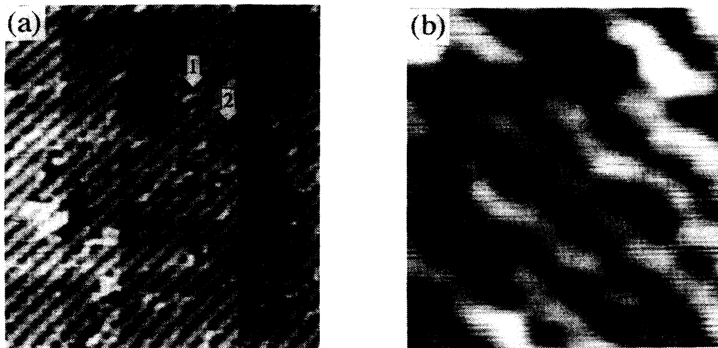

FIG. 1. STM images of Si(001) taken at −1.47-V sample bias and 0.45 nA. (a) An image including various characteristic defects, where typical examples are indicated at 1 and 2 by arrows. (b) An image showing the detailed structure of C defects in the surface layer.

atomic layers. Thus a C defect appears as a protrusion adjacent to a depression. For convenience in the following discussion, we call this protruded region the "bright" side of the C defect, while the depressed region is called the "dark" side.

Figures 2(a) and 2(b) show the occupied STM images of a flat terrace region of the Si(001) surface before and after atom extraction. During atom extraction, the tip of the microscope was scanned parallel to the surface in the diagonal direction from the lower left to the upper right of the image. As indicated at 1 and 2 by arrows in Figs. 2(a) and 2(b), Si atoms in the vicinity of C defects are selectively extracted. Close inspection of the image reveals that in the upper case Si atoms in the neighboring dimer row on the "dark" side of the C defect appear to be extracted, while in the lower case Si atoms in the C defect appear to be extracted and the original C defect becomes a vacancy defect. Since the ease of extraction of atoms is closely related to the binding energy of the atoms and the binding energy depends on the specific local bonding configuration of the atoms,[17] we expect to obtain information about the local energetics around a defect by measuring the extraction frequency of atoms in the region surrounding the defect.

Table I shows results for the frequency of atom extraction, f, from various positions on the terrace region of the Si(001) surface. The position of atom extraction is categorized into three groups depending on the original site from which the atom extraction takes place. The values in the table represent the number of observations of atom extraction from specific positions on the sample surface. The values in parentheses indicate the relative extraction probability as a percentage of all observed extractions. As previously reported,[17] Si atoms are mainly extracted in the vicinity of defects (96%). Among those, the majority of the extract Si atoms are from the positions adjacent to the C defect, while extraction from the vacancy defects is very rare at this voltage. It is important to emphasize here that the C defects where extraction occurs are not usually directly under the path of the tip apex during the the high-voltage scan. This rules out that the modifications might be due to sudden tip motion as the tip travels over the region of different conductivity at the C defect. Thus we believe our observations reflect the energetics of the surface rather than the detailed behavior at the tunnel junction.

Several possible outcomes of atom extraction around a C defect are depicted in Fig. 3, where a small section of surface containing a C defect is illustrated [Fig. 3(a)]. Figures 3(b)–3(d) show possible structures involving extraction of a single-dimer unit from either the C defect or neighboring positions in parallel dimer rows. No such modifications were observed experimentally. Figures 3(e)–3(g) show structures involving the removal of double dimer units. The most frequently observed case in practice is removal of the double-dimer units that form the C defect. We also observe a pronounced anisotropy for removal of neighboring double dimers, with extraction from the "dark" side of the C defect being significantly easier. Triple-dimer extraction at a C defect was only observed in one case and triple-dimer extraction from rows neighboring a C defect was never observed. Other larger types of extraction are rarely observed under the present experimental conditions.

These observations clearly indicate that double-dimer vacancies are more stable structures than single- or

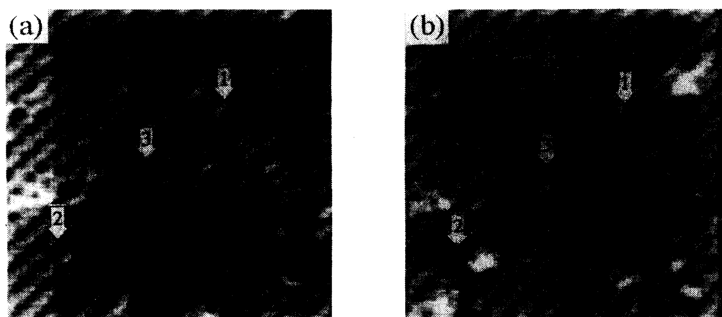

FIG. 2. STM images of Si(001) taken at −1.47-V sample bias and 0.45 nA (a) before and (b) after Si atom extraction with the STM. Si atoms are preferentially extracted in the vicinity of the C defects indicated at 1 and 2.

TABLE I. Frequency of atom extraction, f, from various positions on the terrace of the Si(001) surface, where the sample voltage is fixed to -2.85 V during the atom extraction. The majority of Si atom extractions take place in the vicinity of C defects.

Position of atom extraction	Frequency of atom extraction, f
Normal position	2 (4%)
Position adjacent to dimer vacancy	1 (2%)
Positions adjacent to C defect	46 (94%)

triple-dimer vacancies on Si(001) surface, even when formed artificially. This agrees with STM observations on surfaces with high defect densities, where double-dimer vacancies are found to be particularly stable[18,19] and may play a role in the formation of $2\times n$ structures.[20] The fact that Si atoms in a neighboring dimer row on the "dark" side of the C defect are preferentially extracted suggests that the bonding character in this direction may be weakened due to distortions originated from the atomic rearrangement in the subsurface layers of the C defect. However, since the structure of the C defect is at present unknown, it is not possible to compare this result with theoretical strain calculations yet.

Finally, it is worth noting that the vacancy defects introduced by atom extraction can also induce buckling in adjacent dimers. For example, defect 1 in Fig. 2b induces buckling to the left in the same row and the magnitude of the buckling decays with distance from defect 1. We also observe a local $c(4\times2)$ domain in the lower left part of defect 1. The creation of a $c(4\times2)$ arrangement indicates that the dimer configuration of a row is strongly coupled to the configuration of dimers in adjacent rows, and in case dimers in a row buckle due to defect formation, adjacent rows will favor the antiparallel buckling configuration. Similarly, Wolkow[21] has observed the concerted anitparallel alignment of buckled dimers in neighboring rows at low temperature. In-phase influence of defects in the same row can also be seen between defect 2 and defect 3, where the 11 dimers between the two defects are all buckled, though the exact atomic configuration in the vicinity of the defect 2 is not clearly resolved. In this way, atom extraction also provides a straightforward way to modify the stable dimer configuration locally, and can thus be used to study the surface energetics by creating controlled boundary conditions that give rise to specific dimer structures.

In conclusion, a field-induced atom-by-atom extraction technique has been used to observe the extraction frequency of Si atoms in the region surrounding defects on the Si(001) surface, so that we can obtain information about the local energetics around defects. The dominant type of modification is extraction from the C defect to

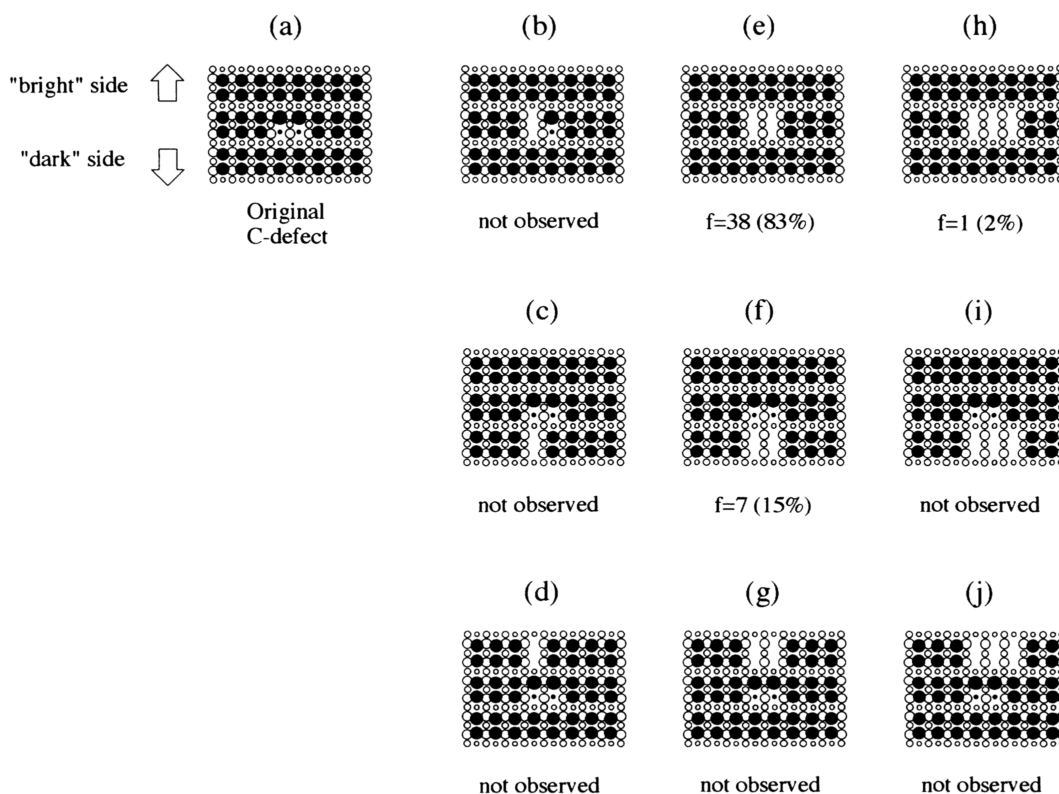

FIG. 3. Structure models illustrating the possible results of atom extraction around a C defect, where the extraction voltage is fixed at -2.85 V. Si atoms are mostly extracted from either the C defect or neighboring dimer row on the "dark" side of the C defect.

form a double-dimer vacancy. We observe an anisotropic extraction behavior from dimer rows neighboring a C defect, with extraction from the "dark" side of the defect being more probable. We attribute these observations to the spatial change of bonding character of atoms in the surrounding region of the C defect, probably due to distortions originated in the underlying layers of the defect. We also observe that these artificially created vacancy defects can induce buckling in the adjacent dimers, so that the correlations between the dimers which determine the local stable dimer configurations were deduced. The sort of atom manipulation described here provides a means of characterizing surface energetics on the atomic scale which is complementary to standard techniques.

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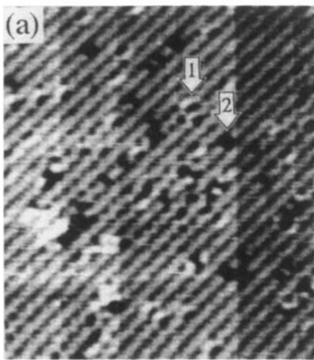

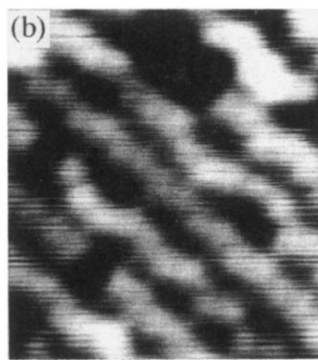

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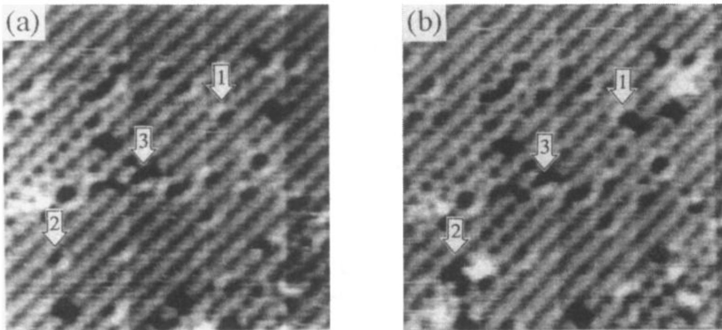

FIG. 2. STM images of Si(001) taken at -1.47-V sample bias and 0.45 nA (a) before and (b) after Si atom extraction with the STM. Si atoms are preferentially extracted in the vicinity of the C defects indicated at 1 and 2.