Interactions between adsorbed Si dimers on Si(001)

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The interactions between adsorbed Si dimers on Si(001) have been studied using scanning tunneling microscopy. These interactions determine the formation of clusters from diffusing dimers. We show that by increasing the tip-sample voltage, we induce transitions between the clusters. These transitions are used to clarify the dimer-dimer interactions and to determine the pathway for the formation of multiple-dimer clusters. [S0163-1829(96)01628-1]

Homoepitaxial growth on Si(001) is a good model system for studying epitaxial growth of semiconductors. A large amount of information about the statics and diffusion of adatoms and adsorbed dimers on Si(001) is known. The diffusion of isolated adatoms has been calculated with model potentials¹ and with *ab initio* methods.^{2,3} These calculations predict the adatom mobility to be so high that scanning tunneling microscopy (STM) measurements cannot reveal isolated adatoms at room temperature. This is consistent with the fact that single adatoms have only been observed at 160 K.⁴ Adsorbed dimers are observed to be immobile at room temperature and for observing their diffusion with STM the sample temperature has to be raised to about 340 K.⁵ Recently the observation of rotations of adsorbed dimers at room temperature has been reported,^{6,7} in accordance with predictions on the basis of *ab initio* calculations.⁸ The dynamic behavior of adsorbed dimers and especially the interactions between them are crucial for the formation of larger clusters from diffusing dimers. However, experimental observations of the processes leading to multiple-dimer clusters are not yet available.

This report describes the interactions between Si dimers adsorbed on top of the substrate dimer rows of a Si(001) surface. These interactions have been deduced from STM observations of transitions between multiple-dimer clusters. We start with a discussion of the rotations of isolated dimers on top of the dimer rows, as it will turn out that these elementary transitions are useful for understanding the more complex transitions in multiple-dimer clusters. Our observations reveal a pronounced tip-sample voltage dependence of the rotation activity of these isolated dimers. This field enhancement of transitions is used as a tool for studying transitions in multiple-dimer clusters. It enables us not only to determine the structures, it also gives insight about how they are formed. It is shown that the interaction of two dimers on top of two neighboring substrate dimer rows can yield two different tetramers. Observations are presented to demonstrate that the interactions in one of these tetramers can be extended to bind more dimers, thus revealing the formation process of large linear clusters.

Experiments are performed in an UHV system with a base pressure of about 5×10^{-11} Torr. Silicon (001) surfaces are prepared by flashing to 1250 °C, yielding the (2×1) reconstructed surface with monolayer height steps. Silicon is deposited at room temperature from a commercial miniature

electron-beam evaporator. A commercial Beetle type STM with a Pt-Ir tip is used for measuring the constant current STM images at room temperature. Movies, made by capturing images at 10 s time intervals, show the surface dynamics at room temperature. This results in a small resolution loss as compared to the individual frames. To label the sites of individual adsorbed dimers and clusters of two adsorbed dimers, we use an extension of the notation for adsorbed Si dimers used by Brocks *et al.*⁸ They are shown together with their notation in Fig. 1.

In Fig. 2, we show, as a function of the bias voltage, the percentage of adsorbed dimers that switch between the *A* and *B* positions between consecutive images. In these positions, the dimers have their bonds parallel and perpendicular to the substrate dimer bonds, respectively. For each bias voltage, 7 dimers in 40 filled state images have been monitored. Although the rotation of adsorbed dimers was reported previously,^{6,7} no influence of the tip-sample interaction had been observed. However, as Fig. 2 shows, we clearly observe an enhancement of the switching activity by the presence of the STM field.

The field enhanced activity of adsorbed dimers is now used as a tool to induce reversible transitions between different configurations of multiple-dimer clusters. With this technique, the interactions between the dimers involved in the transitions can be made visible. We focus on the interactions



FIG. 1. Schematic drawings of the orientations of isolated adsorbed dimers and clusters of two dimers on neighboring substrate dimer rows with their notations.

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FIG. 2. Percentage of dimers that have rotated between consecutive images as a function of the tip-sample voltage.

between dimers adsorbed on neighboring substrate dimer rows. These are relevant upon annealing of a room temperature grown submonolayer, as in that case adsorbed dimers will diffuse mainly along the substrate dimer rows.^{5,9} If two dimers adsorbed on neighboring rows happen to arrive next to each other, dimer-dimer interactions can cause the formation of a cluster. The formation of clusters from diffusing dimers cannot be observed directly at room temperature, because then dimer diffusion is negligible. However, by observing the field enhanced transitions at room temperature, we can analyze the dimer-dimer interactions without raising the temperature. Using these observations, we discuss the structures resulting from the interactions in case of the three possible starting configurations, viz. *AB*, *BB*, and *AA*, as shown in Fig. 1.

The images in Fig. 3, which are taken from a movie, show the formation of structures as a result of dimer-dimer interactions. In Fig. 3(a), all three dimers (1,2,3) are positioned on top of the substrate dimer rows. Between Figs. 3(a) and 3(b) dimer 3 rotates, just as an isolated dimer. Then dimer 3 hops one position along the dimer row, so that dimers 2 and



FIG. 3. Formation of a twin from two individual dimers (a–d). Tunneling conditions: 1.1 nA, 1.2 V.



FIG. 4. Filled (a) and empty (b) state image of a twin (note that a second twin is formed between the capturing of both images). The inset in (b) shows a schematic drawing of a twin (horizontal gray lines indicate new substrate dimer bonds). Interactions between three neighboring *B* dimers (c,d); the dimer in the middle is indicated with an arrow. Tunneling conditions: 0.4 nA, 1.3 V (a); 0.4 nA, -1.0 V (b); 0.4 nA, 1.5 V (c,d).

3 form an AB configuration [see Fig. 3(c)]. In the case of completely isolated dimers, we never observed such a hopping of one position along the dimer row at room temperature. The presence of dimer 2 probably lowered the barrier for the hopping of dimer 3. Apparently dimers on neighboring rows attract each other in order to form lines perpendicular to the substrate dimer rows. The appearance of the adsorbed dimers in the AB configuration is not noticeably different from that of the corresponding isolated dimers. Thus, the dimer-dimer interaction in the AB configuration does not lead to a visible reconfiguration of the structure. As Fig. 3(d) shows, a subsequent rotation of dimer 2 results in a modified BB configuration. The modification of the structure is obvious from the much fainter appearance of the dimers (2,3) of the *BB* configuration, as compared to the appearance of an isolated dimer (e.g., dimer 1). Hence, the interaction leads to a different structure: a tetramer, which we call a "twin." Filled and empty state images of a twin are shown in Figs. 4(a) and 4(b), respectively. Due to the interaction the spacing between the dimers is smaller, which is most clearly observed in the empty state image [Fig. 4(b)]. The smaller spacing can be understood if one assumes that the substrate dimer bonds below the twin dimers are broken, and that new dimer bonds are formed between the substrate atoms in between the twin dimers [see the inset in Fig. 4(b)]. The breaking of the substrate dimer bonds presumably causes a decrease in height of the twin dimers. This can explain their fainter appearance, although changes in the electronic structure should also be taken into account.

It is not possible to extend the twin to a triplet with the same type of interaction. In the two images in Figs. 4(c) and 4(d), which are taken from another movie, the middle of the three *B* dimers forms a faintly visible twin with either of its neighbors, but not with both of them simultaneously. The remaining bright *B* dimer appears to be identical to an isolated one. A repeated switching between these two configurations was observed.



FIG. 5. The formation of a cross (b) from a twin (a). Filled (c) and empty (d) state images of a cross (indicated with an arrow) and an isolated *C* dimer (inside the circle) with a schematic drawing of the cross structure (inset). Tunneling conditions: 1.1 nA, 1.9 V (a,b); 1.0 nA, 1.5 V (c); 1.0 nA, -1.3 V (d).

The third possible two-dimer structure, the AA configuration, leads to a strong reconfiguration of the bonds. The transition from a twin to this structure is shown in Figs. 5(a) and 5(b). The same structure has been indicated with an arrow in the filled and empty state images in Figs. 5(c) and 5(d). Because the substrate dimer rows seem to bend towards the bright spot in between them, we call it a "cross" structure. It can easily be misinterpreted as a two-atom instead of a fouratom structure, because the white spot in between the substrate dimer rows is very similar to the appearance of a dimer on top of the substrate dimer rows. Apart from the rotation of both dimers, the transition in Figs. 5(a) and 5(b) also involves a reconfiguration of the dimer bonds. The single bright dot in the filled state image indicates that a dimer bond is formed between the two atoms in the middle. The two remaining adatoms at the ends are not visible in the filled state image [Fig. 5(c)], while they are in the empty state [Fig. 5(d)]. This illustrates the importance of using both the filled and empty state images. The structural model, which is drawn schematically in the inset in Fig. 5(d), is confirmed by ab initio calculations.¹⁰ The cross structure has a lower energy than two single dimers in the AA configuration, as no stable structures of the latter have been observed. It should be stressed that the adatoms at both ends result from a reconfiguration of the dimer bonds of an AA structure and do not originate from the sticking of single adatoms to a Cdimer. The number of cross structures can be increased by annealing the surface. This easily leads to the wrong conclusion that the number of isolated dimers in between the dimer rows increases. However, using both filled and empty states, the isolated C dimer,¹¹ indicated by the circles in Figs. 5(c)and 5(d) is easily distinguished from the cross structure.

Extended forms of the cross structure have previously been reported and were denoted as diluted dimer rows.^{7,12} The experimental observation of the cross structure shows



FIG. 6. Cross structure with *B* dimer [filled (a) and empty (c) state] transformed to an extended diluted dimer row [filled (b) and empty (d) state]. Schematic drawings of the initial (e) and final state (f) with the intermediate state (g). Tunneling conditions: 0.4 nA, 1.6 V (a,b); 0.4 nA, -1.6 V (c,d).

that the shortest diluted dimer row, formed from two dimers, is stable. We now deduce the pathway for the extension of diluted dimer rows with adsorbed dimers. Figures 6(a) and 6(b) show the extension of the shortest diluted dimer row with two atoms from a B dimer. Empty state images of the same transition are shown in Figs. 6(c) and 6(d). The two corresponding structures are drawn schematically in Figs. 6(e) and 6(f). We have analyzed the time dependent height signal measured with the STM tip positioned right above the end of a diluted dimer row. This height signal switches between two levels, the lower level corresponding to the structure in Fig. 6(b) and the other one to a structure with a dimer on top of the substrate dimer row. As we have observed two significantly different lifetimes for the higher level, we conclude that the transition should involve an intermediate state. Because of the short lifetime of this intermediate state, STM movies only indicate its existence by bright speckles observed at the end of the extended diluted dimer row. The most likely pathway for the extension of the diluted dimer row is the rotation of the B dimer, thus forming the intermediate state in Fig. 6(g), followed by a reconfiguration of the bonds. This model is consistent with the fact that both the short and the long lifetime high level have the same height, because the apparent height of A and B dimers is also identical.

A point of discussion regarding the observed pathways is their validity in the absence of the electric field. For isolated dimers, however, the observed field effect is similar to the effect of raising the temperature, as predicted using *ab initio* calculations.^{8,10} As the transitions observed in clusters also involve these basic transitions, it can be expected that they are also enhanced upon raising the temperature. Furthermore, the structures resulting from transitions observed by scanning at high bias voltages are also observed on surfaces scanned for the first time at low bias voltages (e.g., 1.1 V). This shows that the specific bond reconfigurations also occur under zero-field conditions. Thus, the high bias voltages only enhance the activity of individual adsorbed dimers and dimers in clusters without creating new structures. The relative frequencies of occurrence of certain configurations, however, have to be interpreted with some care.

We conclude that the STM field strongly influences the transition activity of dimers adsorbed on top of the substrate dimer rows. The observation of similar field enhanced transitions in multiple-dimer clusters is demonstrated to be a powerful tool for analyzing dimer-dimer interactions. The interaction depends on the relative orientation of the dimers on neighboring dimer rows. Nonparallel dimers (*AB* con-

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figuration) show hardly any interaction. However, dimers in an AA or BB configuration interact, resulting in the formation of a cross and a twin structure, respectively. The previously undescribed twin structure is difficult to recognize because of its faint appearance. The interaction forming a twin cannot bind more than two dimers to form larger clusters. The cross structure is a short form of the so-called diluted dimer rows. It requires special attention because this starting point for the growth of a long diluted dimer row is easily misinterpreted as a single dimer in between the substrate dimer rows. The corresponding dimer-dimer interaction can be used to bind more dimers in the linear structure. The pathway for the extension of this structure from diffusing dimers has also been deduced.

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