# Room-temperature growth of submonolayers of silicon on Si(001) studied with scanning tunneling microscopy

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Room-temperature deposited submonolayers of silicon on Si(001) are investigated using STM. The observed structures and the mechanisms leading to their formation are discussed. Isolated ad-dimers in different geometries are described and a kinetic model for their formation is deduced. It is shown how further growth occurs via the formation of 3-atom clusters, which act as nucleation centers for the formation of two types of linear structures. One of the line types is formed in the [110] direction, and has been observed before. The other is in the [310] direction. At a coverage of nearly 0.2 ML a kind of random network consisting of segments of the two types of atomic lines is formed. Above 0.2 ML coverage these lines are converted into epitaxial dimer rows. A pathway for this conversion is proposed on the basis of experimental observations. [S0163-1829(97)11107-9]

### I. INTRODUCTION

The homoepitaxial growth on Si(001) has been used as a model system for studying epitaxial growth for quite a long time. Eaglesham, Gossmann, and Cerullo<sup>1</sup> have shown that there exists a maximum layer thickness for epitaxial growth, which is reduced if the temperature is lowered. They estimated the epitaxial thickness for room-temperature growth of silicon on Si(001) to be 10–30 Å. This indicates that it should be possible to grow a few monolayers of silicon epitaxially on Si(001) at room-temperature. The room temperature growth of silicon on Si(001) has been studied with a number of techniques such as TEM,<sup>2</sup> Rutherford backscattering/channeling,<sup>3,4</sup> and low-energy electron diffraction.<sup>5–7</sup> These results led to some controversy as to whether the first layers of silicon on Si(001) grow epitaxially at room temperature or not.

The observation techniques mentioned before are global in the sense that they only allow for the assessment of the epitaxial quality of atomic layers as an average property of those layers. For a microscopic analysis of the processes controlling epitaxial growth scanning tunneling microscopy (STM) is better suited. Although some attention has been paid to room-temperature growth of submonolayers,<sup>8,9</sup> STM studies have mainly been focused on surfaces prepared at elevated temperatures, where ad-dimers are mobile.<sup>10,11</sup>

At room temperature the growth mode is significantly different from that at elevated temperatures. Because ad-dimers are immobile at room temperature all structures are necessarily formed from the addition of single adatoms. Adatoms are diffusing too fast to observe them with STM at room temperature.<sup>12,13</sup> How these adatoms aggregate to form clusters of two, three, or more atoms is still not very well understood. STM experiments at 160 K have nicely demonstrated the formation of ad-dimers from adatoms,<sup>14</sup> although at that temperature the diffusion of adatoms along the rows is not activated. Therefore, it is still unknown what processes occur in case the adatom motion is fully activated.

While there is still discussion about the early stages of

growth, even less is known about the more complicated structures and processes at higher coverages. So far, a few nonepitaxial structures have been observed.<sup>9,15</sup> In these structures the dimer bonds and positions of the dimer atoms are different from those in a epitaxially well ordered complete overlayer. The energies of ad-dimers and various other structures have been calculated<sup>16–18</sup> in order to explore possible pathways for the evolution of the structures.

The experimental data available to date have not enabled a complete analysis of all types of clusters and the various binding sites for adatoms at these clusters. A thorough analysis of this problem is needed to understand the complete picture of room-temperature growth of silicon on Si(001). Microscopic knowledge of the growth processes is needed to determine the pathways to the formation of epitaxial layers. The transition rates of the critical steps in these pathways determine the epitaxial quality.

In this paper we discuss the evolution of the structures during room temperature growth of a submonolayer. The details of the experimental techniques are outlined in Sec. II. The increasing complexity of the structures for increasing coverage is shown in the STM images in Fig. 1. First we will discuss the features observed at low doses. In these early stages of the growth nearly all atoms are incorporated in two-atom clusters, i.e., dimers. We discuss the observed binding sites for ad-dimers and present a model for their formation. The dominating influence of kinetics incorporated in this model also sheds new light on the recent discussion<sup>19</sup> about the stability of the different ad-dimer bonding geometries. Then we describe the formation of the 3-atom cluster, which is the next step in the growth process. As we will show all different ad-dimer geometries observed on the surface can be converted to this cluster by the addition of one adatom. Subsequently, the formation of larger structures and the mechanisms causing their increasing complexity are discussed. The interaction between dimers causes them to line up in linear structures. This is the dominant process controlling the island morphology. Finally, we show that these linear structures can be transformed into epitaxial structures. Experimental evidence for the pathway involved in this tran-

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FIG. 1. Empty-state STM images with coverages of 0.012 ML (a), 0.05 ML (b), 0.18 ML (c), and 0.20 ML (d). The layers have been deposited in 10 min (a),(b),(d) or 15 min (c). Tunneling conditions: 0.4 nA, -1.3 V (a)–(c); 1.0 nA, -1.5 V (d).

sition is also discussed. The analysis of the complete growth process has been based on a large number of images obtained from samples with various coverages. The analysis covers nearly all structures observed in the experiments. All other structures that have been observed did not seem to be relevant for the growth process, as they only occurred occasionally.

### **II. EXPERIMENT**

Experiments are performed in a UHV system with a base pressure of  $5 \times 10^{-11}$  Torr. A commercial Beetle type STM<sup>20</sup> with a Pt-Ir tip is used for measuring the constant current STM images. Movies, made by capturing images at 10-s time intervals, show the surface dynamics at room temperature. For all dynamic processes observed with the STM we need to keep in mind that they may be influenced by the electric field. Nevertheless, they give useful indications for possible pathways with a reasonable transition rate at or slightly above room temperature, as was shown in a previous study.<sup>21</sup> Silicon (001) surfaces are prepared by flashing to 1250 °C, yielding the  $(2 \times 1)$  reconstructed surface with monolayer height steps. Deposition at room temperature is performed at least 4 h after flashing the sample. As waiting for a longer period does not change the results, the sample temperature is close enough to room temperature. Silicon is deposited from a commercial miniature electron-beam evaporator.

### **III. ISOLATED AD-DIMERS**

The smallest immobile islands created during roomtemperature growth on Si(001) are ad-dimers. For denoting the different binding geometries of the most probable sites we use the notation shown in Fig. 2. We have been able to identify these dimer configurations in our STM images. No



FIG. 2. Four different binding geometries (A-D) for ad-dimers.

different dimer configurations have been observed in these experiments. The *A* and *B* dimers, which reside on top of the dimer rows, are well known and easily identified by the direction of their elongation [see Figs. 3(a), (b)]. The appearance of the *C* and *D* dimers in STM images requires special attention as they have not been described previously.

We have never observed isolated D dimers. This is in accordance with the predictions based on *ab initio* calculations.<sup>16</sup> To show what an isolated D dimer might look like, we present in Figs. 3(c), (d) clusters that contain D dimers. Nearly all D dimers we observe have a neighboring B dimer (see, e.g., dimer  $D_3$ ). This corresponds to the DB structure required for the formation of an epitaxial overlayer. Dimers  $D_1$  and  $D_2$  form a cluster together and show the appearance of D dimers without a neighboring B dimer.

Three examples of the structure that we have identified as the *C* dimer are shown in Figs. 3(a,b). While they are clearly visible in the empty state image [Fig. 3(b)], their appearance in the filled-state image [Fig. 3(a)] is even fainter than that of the substrate dimers. In comparison with the *D* dimers  $D_1$ and  $D_2$  [Figs. 3(c), (d)], the structures  $C_1$ - $C_3$  in Figs. 3(a),



FIG. 3. Filled-state image (a) showing an A dimer, a B dimer, and three C dimers  $(C_1-C_3)$  together with empty-state image (b), where the A dimer has rotated back to the B orientation. Filled- (c) and empty-state (d) images where three D dimers are indicated as  $D_1-D_3$ .  $D_3$  looks different because there is a B dimer on top of the neighboring dimer row. Tunneling conditions: 0.4 nA (a)–(d) and 1.3 V (a), (c); -1.3 V (b); -1.15 V (d).



FIG. 4. Filled- (a), (c) and empty-state (b), (d) images of C dimers with perfect (a), (b) and imperfect (c), (d) buckling like a circle of adatoms. Tunneling conditions: 1.5 nA, 1.3 V (a); 1.5 nA, -1.3 V (b); 1.1 nA, 1.3 V(c); 1.1 nA, -1.3 V(d).

(b) have an aspect ratio much closer to unity. Nevertheless, we observe that their long axis is directed perpendicular to the dimer rows. Similar differences are observed between B and A dimers. This supports the identification of the structure as a dimer located in between the dimer rows with the dimer bond parallel to the substrate dimer bonds, i.e., as a C dimer. In the filled-state image [Fig. 3(a)] the C dimers are characterized by a surrounding "circle" of visible substrate atoms. The interaction between dimers along the substrate dimer rows causes an anticorrelated buckling which is visible over a range of about six dimers at both sides of the structure. In the filled-state images the C dimers appear in different forms. Most C dimers do not exhibit a circle of visible substrate atoms as perfect as that shown in Fig. 4(a). Instead, we often observe imperfect circles, where one or two of the atoms forming the circle seem to be missing [Fig. 4(c)]. The empty-state image in Fig. 4(d), however, shows that they are still there. The exact origin of these imperfections is not yet clear.

From the STM images the abundances of the structures have been determined for different coverages [see Fig. 5(a)]. For low coverages (i.e., less than one dimer per substrate dimer row) the numbers of isolated A, B, and C dimers increase linearly with coverage. At a coverage of about 0.01 ML [see Fig. 1(a)] the formation of multiple-dimer clusters reduces the rate of increase of the number of isolated addimers. A and B dimers have been observed to transform into each other at room temperature.<sup>21,15,19</sup> Hence, it is justified to assume that these populations are in thermodynamic equilibrium and, therefore, we will often address them as the A/B population. From the ratio B:A of 10:1 the energy difference of the sites can be estimated. This yields a 60-meV lower energy for the B site compared to the A site. This near degeneracy of A and B dimers is in accordance with theoretical calculations.16-19

Of all isolated ad-dimers 67% are in the *C* position [see Fig. 5(b)]. If we assume that the *C* dimer population is in thermodynamic equilibrium with the A/B population we find an energy difference of only 20 meV between the *C* and A/B sites. This contradicts *ab initio* calculations<sup>17,18</sup> that predict an energy difference larger than 100 meV. There are, however, a number of indications that the abundance of the *C* dimers is kinetically determined. First of all, we did not observe with our STM any switching of isolated ad-dimers between the *C* position and the A/B positions. Secondly, the



FIG. 5. (a) Density of isolated A, B, and C dimers in arbitrary units as a function of coverage. Straight lines indicate the linear increase with coverage for the lower three coverages. (b) The percentage of isolated dimers in the C position as a function of coverage. The line corresponds to a ratio of 2/3.

percentage of isolated ad-dimers in the C positions matches the exact value of 2/3 remarkably well. This strongly suggests the following, kinetically determined origin for the distribution. According to *ab initio* calculations<sup>12,13</sup> the adatoms will diffuse on top of the dimer rows, making frequent side trips to the more stable sites at either side of the rows. Diffusion across the dimer rows is not activated at room temperature. Therefore, the adatoms remain on the dimer row on which they are deposited. We now assume that two adatoms separated by more than one dimer row cannot form a dimer and that the type of dimer formed only depends on the row on which the second adatom is deposited. Then, dimers are formed either from two adatoms on neighboring dimer rows or from two adatoms on the same row. This results in a chance of 2:1 that the second adatom is deposited on a neighboring row instead of on the same row. If the adatoms meet on the same dimer row A/B dimers are formed. If they meet on neighboring rows a C dimer is formed. This causes 2/3 of the dimers to be formed in the C position as observed experimentally.

This model for the dimer formation may seem to contradict the observations of Wolkow,<sup>14</sup> who described the exclusive formation of A/B dimers from adatoms on neighboring dimer rows at a temperature of 160 K. The apparent interaction between adatoms on different rows was attributed to strain effects. However, these subtle strain effects will be washed out at room temperature. Consequently, at room temperature other interactions dominate the formation of dimers.

As discussed before the abundances of A/B and C dimers are kinetically determined. Therefore, room-temperature deposited submonolayers cannot reveal any information about the energy differences of these sites. Annealing experiments may be performed to determine the thermodynamic stability



FIG. 6. Filled- (a) and empty state (b) images of a three-atom cluster with a schematic drawing (c) of a *C* dimer with the two possible binding sites (1,2) for an adatom to form a stable three-atom cluster. Tunneling conditions: 0.3 nA, 1.3 V (a); 0.3 nA, -1.3 V (b).

of the isolated ad-dimers. For interpreting such experiments it has to be realized that the *C* dimers may still be frozen in their positions while the diffusion of A/B dimers is already activated and causes the formation of clusters. Annealing experiments<sup>19</sup> have been reported to result in an increase of the number of dimers in between the substrate dimer rows. This observation is, however, probably due to the formation of tetramers, which are easily misinterpreted as isolated dimers.<sup>21</sup>

#### **IV. THREE-ATOM CLUSTERS**

As ad-dimers are immobile at room temperature, stable nuclei can only grow by the addition of adatoms. The first step in this growth process is the formation of a three-atom cluster by adding one adatom to an ad-dimer. We only observed one type of stable three-atom cluster, an example of which is shown in Figs. 6(a), (b). In this cluster an atom is bound next to a C dimer at site 1 or 2 in the schematic drawing in Fig. 6(c). In this manner all three atoms are positioned on one line perpendicular to the substrate dimer rows. Our observation that this is the only stable three-atom cluster is corroborated by the work of Yamasaki, Uda, and Terakura,<sup>18</sup> who did not find other stable three-atom clusters in their calculations. In filled-state images the C dimer of the three-atom structure is now also visible as a bright spot in contrast to its appearance as an isolated ad-dimer. The adatom of this structure is invisible in the filled-state images. This adatom is indicated with an asterisk in the empty-state image, Fig. 6(b).

The most straightforward mechanism for the formation of a three-atom cluster is the sticking of an adatom to a Cdimer. This adatom can arrive at either side of a C dimer via diffusion along the dimer rows next to the C dimer. Experimental evidence for this pathway is the fact that we observed several C dimers in filled-state images turning bright. Because we do not have empty-state images of these transitions, the addition of the extra atom has not been observed directly. The observed increase in brightness of the C dimer,



FIG. 7. Empty-state images from a movie and schematic drawings demonstrating the formation of a three-atom structure from a *B* dimer and an invisible extra adatom before (a) and after formation (b). Subsequent rotation of dimer  $B_2$  to the *A* configuration (c) enables comparison of an atomically resolved *A* dimer with a three-atom structure. [In (b) dimer  $B_3$  from (a) and (c) is in the *A* configuration.] Tunneling conditions: 0.4 nA, -1.7 V.

however, is exactly the visible effect in filled-state images if a C dimer catches an adatom, as can be seen from the comparison of the C dimer appearances in Figs. 4(a) and 6(a).

A more surprising observation is the existence of a second pathway for the formation of the three-atom cluster. Here, an A/B dimer is converted into a three-atom cluster. In this case the transition is more complex because the dimer bond of the A/B dimer is broken during the transition. The three images in Fig. 7 showing this conversion are obtained from an STM movie. In Fig. 7(a) we observe three *B* dimers on one dimer row. One of these *B* dimers ( $B_1$ ) catches an extra adatom and forms a three-atom cluster as shown in Fig. 7(b). That this structure is indeed a three-atom structure is confirmed by Fig. 7(c). In contrast to the *A* dimer, the three-atom structure exhibits one elongated spot and one spot that is similar to those of the *A* dimer. The elongated spot originates from the *C* dimer and its midpoint is visibly shifted towards the middle of the trough between the substrate dimer rows.

Both conversion processes starting from A/B or C dimers occur with more or less equal probability. Forming threeatom clusters exclusively from either C or A/B dimers would change the ratio of their abundances of 2:1. For a coverage of about 0.012 ML, where 15% of the atoms have formed a three-atom cluster, the abundance of isolated addimers in the C position is still 2/3. Using only the C dimer for forming three-atom clusters would have caused a small but significant decrease of the C dimer abundance (from 67% to 63%). The absence of any change in the ratio of the abundances indicates roughly equal efficiencies for forming three-atom clusters by sticking adatoms to either C or A/Bdimers. This also suggests that A/B dimers cannot be transformed into three-atom clusters by atoms diffusing on the same dimer row. In that case the capture area for atoms causing the transformation only comprises the two neighboring dimer rows for both A/B and C dimers. This assumption is confirmed by *ab initio* calculations,<sup>18</sup> as these calculations did not yield any evidence for interactions between adatoms and A/B dimers on the same dimer row.

# V. DILUTED DIMER ROWS

The three-atom clusters described in the preceding section act as templates for forming larger nonepitaxial structures. They are extended by sticking adatoms in line with the atoms of the cluster at either end of the structure. If adatoms are bound at both sides of a C dimer [sites 1 and 2 in Fig. 6(c)], a four-atom cluster is formed. In a previous study<sup>21</sup> we have demonstrated that this structure, which we called a "cross structure," is formed from two dimers on neighboring substrate dimer rows. In our present study we also observed the cross structure. Because the submonolayers in this study are grown at room temperature, where ad-dimers are immobile, we conclude that the cross structure can also be built up atom by atom. The general form of the structure obtained by extending the three-atom cluster with an arbitrary number of atoms is a line of atoms along the [110] direction, i.e., perpendicular to the substrate dimer rows. This [110] line consists of a number of C dimers in neighboring troughs between the substrate dimer rows. Either end of the [110] line can consist of a C dimer or an adatom. These structures have been described before<sup>9,21,15</sup> and are denoted as diluted dimer rows. The process governing their formation is analogous to the surface polymerization reaction described for Al on Si(100).22

A puzzling question is the difference in brightness between isolated *C* dimers and *C* dimers in these diluted dimer rows. We propose two explanations, based on the geometries of the two structures obtained from *ab initio* calculations.<sup>17</sup> First, the dimer bond for the *C* dimer in the row is much shorter than that of the isolated dimer. We expect the resulting increased overlap of the atomic orbitals to lead to a higher density of states above the dimer, and hence to a brighter appearance in the STM images. Second, the dimer in the row is buckled, whereas the isolated one is symmetric. Naturally, the upwards buckled atom appears higher than that of a symmetric dimer. This effect can even be enhanced by a charge transfer from the downwards buckled atom to the upwards buckled atom. The dimer appears symmetric in the image due to temperature activated switching.

## VI. DIMER ROWS ALONG [310] DIRECTIONS

Apart from the known diluted dimer rows we observed a linear structure that also consists of C dimers. The structure is formed along [310] and its symmetry related directions. It is very common at doses above 0.05 ML. A special V-shaped example consisting of two connected linear segments is shown in Figs. 8(a), (b).

The formation of the rows along the [310] directions can be explained if we assume a precursor state in which an adatom is bound near a *C* dimer in one of the four metastable binding sites (1-4) in Fig. 8(c). These sites may originate from the strain induced by the presence of the *C* dimer. The interaction of adatoms bound at these sites with other diffusing adatoms will lead to the formation of new dimers. Analogous to the formation of isolated ad-dimers an A/B dimer



FIG. 8. A V-shaped row of *C* dimers in the [310] directions; filled state (a) and empty state (b). The four metastable binding sites (1)-(4) for adatoms involved in the formation of [310] lines are schematically depicted in (c). Tunneling conditions: 0.4 nA, 1.3 V (a); 0.4 nA, -1.3 V (b).

can be formed with an atom diffusing on the same dimer row. An atom diffusing on the neighboring dimer row will yield a new C dimer and extend the row along the [310] direction.

We have no direct evidence for the existence of the precursor state, but we have observed "clusters" of precursor states, an example of which is shown in Fig. 9. We expect that the adatom binding sites of the precursor state are not stable at room temperature, but that they have nevertheless an increased occupancy during the growth. The combination of two precursor states shown in Fig. 9 does become stable at room temperature.

The *C* dimers in the [310] chains are only faintly visible in the filled-state images, as in the case of isolated *C* dimers. Therefore, the neighboring *C* dimers in these lines do not seem to influence the *C* dimer bonds as strongly as in the case of the diluted dimer rows.

We can now describe the growth up to doses of about 0.2 ML. At very low doses (< 0.05 ML) we get the structures described in Secs. III and IV. When growth proceeds further, adatoms stick to existing structures, forming one of the linear structures described in Secs. V and VI. Other structures are relatively rare. Because extension of the linear structures occurs either in the [110] or in the [310] direction, we end up with a kind of random network of atomic line segments in



FIG. 9. Filled- (a) and empty-state (b) images with a schematic drawing [inset in (a)] of a cluster of two three-atom precursor states. Tunneling conditions: 0.4 nA, 1.3 V (a); 0.4 nA, -1.3 V (b).



FIG. 10. Diluted dimer row ending with *BD* epitaxial segment (a) and one ending with a twin (b). The straight lines in (a) are plotted to indicate the edges of a substrate dimer row, which can be deduced from the position of the vacancy in this row at the lower right end. Tunneling conditions: 0.4 nA, -1.3 V.

these directions, with relatively open areas in between them [see Fig. 1(c)]. At this stage of the growth deposited atoms are rapidly captured by one of the numerous (metastable) binding sites of the network.

### VII. TRANSITION TO EPITAXIAL STRUCTURES

After deposition of nearly 0.2 ML the majority of the deposited material still occupies nonepitaxial binding sites, since most of the ad-dimers in the network are in the Cposition. Further growth now causes a conversion of the majority of nonepitaxial diluted dimer rows into epitaxial dimer rows. At 0.18-ML coverage [see Fig. 1(c)] already a few diluted dimer rows are observed to be partially converted into epitaxial dimer rows. A pronounced increase in the abundance of epitaxial structures is obvious from the comparison of Fig. 1(c) and Fig. 1(d), which originate from different experiments. The abundance of epitaxial structures with at least 4 atoms increases from 38 to 50% while the dose differs only 0.02 ML. The fact that a substantial conversion to epitaxial structures does not take place at an earlier stage of growth indicates that there exists a considerable barrier for this transition.

We observed the following characteristics of the partially converted diluted dimer rows: (1) apart from a few exceptions, where diluted dimer rows contain a single epitaxially oriented dimer, the smallest epitaxial segments always contain two dimers; (2) the conversion occurs exclusively at the ends of the diluted dimer rows; (3) epitaxial segments with the outer dimer being a *B* or *D* dimer are both observed. An example of one ending with a *D* dimer is presented in Fig. 10(a).

A pathway accounting for the above-mentioned experimental observations is depicted in Fig. 11. It initiates by forming a *B* dimer from an atom of the outer *C* dimer with the adatom at the end of the diluted dimer row. This process has been observed with STM previously.<sup>21</sup> Repeating the process at the end of the remaining diluted dimer row then creates a modified *BB* structure, which we previously denoted as a "twin."<sup>21</sup> Finally, a collapse of this twin structure leads to an epitaxial *BD* segment. This conversion path yields a sequence ending with: *C*, adatom, *B*, *D*.

The conversion path is fairly complex and the major question is whether the kinetic barriers for the steps involved in



FIG. 11. Pathway for the conversion of diluted dimer row ends (a) into epitaxial segments (d). A three-atom cluster (e) is converted into a cross structure (f) by the addition of an extra adatom. This structure can transform into a twin structure (g).

the conversion process are not too large. At present we do not have a sequence of consecutive images showing the complete conversion process. However, we did observe all the individual steps.

The formation of a B dimer at the end of a diluted dimer row according to the first step in the conversion path [from (a) to (b) in Fig. 11] has been observed earlier,<sup>21</sup> but in these observations the transition activity was clearly enhanced by the presence of the electric field. The proposed conversion path requires the consecutive occurrence of two of these transitions to form a twin structure at the end of the diluted dimer row. This may reduce the conversion rate. However, the fact that we have observed a few diluted dimer rows ending with a twin structure [see Fig. 10(b)] proves that the first two steps of the conversion path [see Figs. 11(a)-11(c)] do exist. Furthermore, we have observed that about 4% of the atoms form twin structures at 0.18 ML coverage. This demonstrates that under growth conditions the conversion to twin structures does occur at a reasonable rate. These twins can only be formed from a diluted dimer row, i.e. in a process similar to the first two steps of the conversion path, which is concluded from the following reasoning. Growth is performed at room temperature and, therefore, occurs exclusively by the addition of single adatoms. This means that the precursor for the twin structure with four atoms should be a three-atom structure. Because we only observed three-atom structures with a C dimer, the most likely pathway [see Figs. 11(e)-11(g) is the formation of a cross structure (a diluted dimer row with four atoms), which is then converted to a twin structure. The latter process is identical to the first part of the conversion to an epitaxial segment.

Once a twin structure has been formed, an epitaxial segment is formed [compare Figs. 11(c), (d)] by a collapse to a *BD* structure as shown in the STM images in Fig. 12. The two *B* dimers of one of the twins in Fig. 12(a) are indicated with arrows. After the collapse [see Fig. 12(b)] the distance of the dimers has been halved, in accordance with the formation of the *BD* epitaxial segment. Similar epitaxial structures with two dimers are frequently observed on roomtemperature-grown submonolayers. This shows the existence of the transition under growth conditions. The transition of the twin structure to the *BD* cluster has recently been studied with *ab initio* methods.<sup>18</sup> The transition mechanism explored in these calculations has an activation energy of 1.6 eV. This



FIG. 12. Sequence of transitions from an STM movie, showing the formation of an epitaxial structure (b) from a twin (a). Dimers of the twin and the epitaxial structure are indicated with arrows. The extra adatom (indicated with an asterisk) from a neighboring structure is attached to the epitaxial segment in (c). Tunneling conditions: 0.4 nA, -1.6 V.

activation energy renders the transition mechanism practically forbidden at room-temperature, while we do observe *BD* clusters after room-temperature growth. Apparently, there should exist an alternative conversion mechanism with a lower activation barrier.

The proposed conversion path accounts for the formation of epitaxial segments ending with a *D* dimer, which is observed to be the case for at least 50% of the observed segments. It does not explain the form of the other epitaxial segments, which end with a *B* dimer. These segments may be formed along the path proposed by Brocks and Kelly.<sup>17</sup> This conversion path initiates with the arrival of an adatom and always results in a segment ending with a *B* dimer.

The conversion path for the formation of epitaxial segments is expected to be very sensitive to the local geometry. Local modifications of the strain distribution induced by neighboring structures may facilitate the occurrence of the complex transitions to epitaxial structures at higher coverages. This explains the rapid increase of the abundance of epitaxial structures at about 0.2 ML. Further investigations are needed to quantify these local strain effects.

We often observe single adatoms bound at the end of epitaxial segments but they are not a clue for the conversion process as they do not necessarily originate from the conversion process. This is demonstrated in the transition that occurred between Figs. 12(b) and 12(c). Here, an adatom bound nearby has moved and is finally bound alongside the D dimer of the epitaxial structure. Epitaxial segments both with and without an extra adatom have been observed. As the transition in Fig. 12 shows, the extra adatoms can originate from nearby structures. Furthermore, atoms deposited afterwards may also bind at these sites.

### VIII. CONCLUSIONS

The evolution of structures during room-temperature deposition of submonolayers of silicon on Si(001) has been presented. The data are obtained by a careful analysis of all features observed in numerous STM images of the Si(001) surface after deposition of different coverages. All observed features have been described except for the defects and those structures that occur in such small numbers that they do not seem to be of importance for the growth process. The evo-



FIG. 13. Overview of the evolution of the relevant structures during room temperature growth of silicon on Si(001).

lution of the relevant structures during growth is schematically depicted in Fig. 13. The growth starts with adatoms forming ad-dimers. We found that adatoms diffusing on the same dimer row form A or B dimers, while adatoms on neighboring dimer rows yield C dimers. Stable three-atom clusters with all atoms aligned along one row perpendicular to the substrate dimer rows can be formed if adatoms stick to A, B, or C dimers. These stable three-atom clusters form the precursor state for the lines of dimers along the [110] direction (diluted dimer rows). Apart from the diluted dimer rows, lines of dimers can also be formed along the [310] and its symmetry related directions. The three-atom precursor state for these lines is probably the one depicted in Fig. 13. Its adatom binding site, however, is not as stable as that in the three-atom cluster which has all atoms in one line. Both the [110] dimer lines and the [310] lines are compatible with each other in the sense that structures consisting of connected segments of both line types can be formed. Finally, a transition to epitaxial structures occurs by the formation of epitaxial segments in diluted dimer rows. Based on STM observations a possible pathway for this conversion process is proposed. The shortest diluted dimer row that can be converted to an epitaxial structure consists of a C dimer with two atoms (cross structure). Its conversion into an epitaxial structure occurs via the twin (modified BB cluster) as shown in Fig. 13.

Thus we have shown that epitaxial structures are formed during deposition of submonolayers of silicon on Si(001). For growing thicker layers the probability for adatoms to step down at the step edges further influences the epitaxial quality. The room-temperature activation of that process requires a separate study.

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