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Citation for published version (APA):

Brocks, G., & Kelly, P. J. (1996). Dynamics and nucleation of Si ad-dimers on the Si(100) surface. *Physical Review Letters*, 76(13), 2362-2365. <https://doi.org/10.1103/PhysRevLett.76.2362>

DOI:

[10.1103/PhysRevLett.76.2362](https://doi.org/10.1103/PhysRevLett.76.2362)

Document status and date:

Published: 25/03/1996

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Dynamics and Nucleation of Si Ad-dimers on the Si(100) Surface

G. Brocks and P. J. Kelly

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

(Received 24 October 1995)

The motion of Si ad-dimers on the Si(100) surface is studied by means of *ab initio* (Car-Parrinello) molecular dynamics. We observe dynamic buckling of the dimers and the rotation of a single ad-dimer on top of a substrate dimer row. A model is presented for the structure and the formation of the recently observed "dilute" ad-dimer rows, which explains their one-dimensional growth. We propose that these rows are intermediate structures for the strongly anisotropic epitaxial growth on Si(100).

PACS numbers: 68.35.Fx, 68.35.Md, 73.20.Hb

Of all surfaces of covalently bonded materials, the Si(100) has come to be the surface of choice for studying the microscopic processes which govern crystal growth such as adsorption, nucleation, and island formation. Application of the new technique of variable temperature scanning tunneling microscopy (STM) to study the dynamics of adsorbed species directly in real space [1–6] is revealing a much more complex picture than what is usually assumed when the growth is modeled on a microscopic scale [7,8].

Theoretical modeling has become much more powerful since the introduction of Car-Parrinello techniques enabling molecular dynamics to be performed from first principles [9]. Calculations of the energetics and mobility of Si adatoms [10] and ad-dimers [11] were used to identify the diffusing species observed by Dijkkamp, van Loenen, and Elswijk [1] as Si ad-dimers. These calculations also predicted a possible rotational motion of the Si ad-dimer between two inequivalent, but energetically almost degenerate structures [11]. This prediction was recently confirmed by Zhang *et al.* [3] and independently by Bedrossian [4,5] with STM experiments.

The most basic question that remains to be addressed is how ad-dimers (or ad-dimers and adatoms) combine to form larger units and start the actual growth. An important piece of information comes from an annealing experiment carried out by Bedrossian [4,5]. Upon heating up to a temperature $T = 400$ K, he observed Si ad-dimers in "dilute" rows, in which the Si adatoms seem to be in nonepitaxial positions. A major problem with STM is that it gives us information about the electronic local density of states (LDOS), but the underlying atomic structure is only accessible via theoretical modeling. In this paper, we will calculate structures and use the associated LDOS to make a connection with STM images. Starting from an isolated Si ad-dimer, we will present a model for the formation and structure of the dilute rows of Si ad-dimers. We propose that such dilute dimer rows play an important role in promoting the observed strongly anisotropic epitaxial growth [12].

In studying the surface dynamics, we use the Car-Parrinello scheme of *ab initio* molecular dynamics; min-

imum energy structures are obtained using the same scheme in a quenching mode [9]. Parameters such as plane wave kinetic energy cutoff and Brillouin zone sampling have been chosen as in our previous calculations [10,11]. Such parameters can be varied to estimate the reliability of the computed results [13]. For the present study we estimate that energy differences have converged to approximately 0.1 eV.

Figure 1 presents four optimized structures of Si ad-dimers on the Si(100) surface, as calculated in a $p(4 \times 4)$ surface unit cell [14]; all four represent local minima. It is clear from the bond lengths listed in Fig. 1 that the dimer reconstruction of the substrate is not broken in any of the structures. The relative energies of the structures which we denote 1a, 1b, 1c, and 1d are 0.0, 0.01, 0.31, and 1.11 eV, respectively [15]. Positioning the ad-dimer on top of a dimer row of the underlying substrate as in structures 1a and 1b yields the lowest energy despite the small bond angles formed in these cases. In these favorable configurations the Si-Si bonds are in the range 2.3–2.4 Å. Some of the Si-Si bonds associated with the less stable configurations, where the ad-dimer is positioned between the dimer rows of the substrate as in structures 1c and 1d, are strained and in the range 2.5–2.6 Å. Apparently, the more favorable

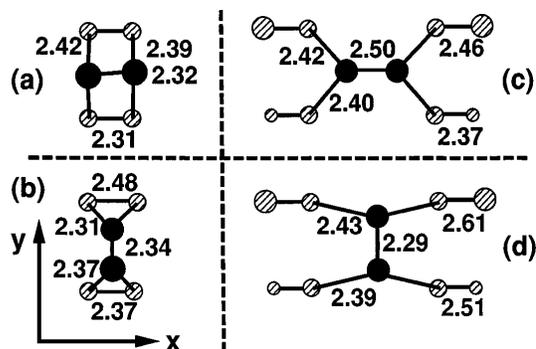


FIG. 1. Schematic drawing of optimized structures of Si ad-dimers on the Si(100) surface. The black circles represent the Si adatoms, where the size represents the height, and the shaded circles represent the atoms of the Si(100) substrate. The numbers give Si-Si bond lengths in Å.

bonding angles in structures 1c and 1d do not compensate for the increase in strain energy [16]. The small energy difference between structures 1a and 1b is within the error bar of the calculation. Indeed, experiment seems to indicate that structure 1b is more stable [3–6]. To reduce the theoretical error bar significantly would require a substantially larger calculation beyond the scope of the present paper [13]. Moreover, at finite temperatures one should compare free energies, since there might be a non-negligible contribution from the entropy on this energy scale.

A more direct comparison with the STM observations can be made by calculating the local density of states $\rho(\mathbf{r}, \varepsilon)$ [17]. Since the experimental energy resolution is finite, we calculate an average LDOS $\bar{\rho}(\mathbf{r}, \varepsilon)$ by convoluting the theoretical LDOS $\rho(\mathbf{r}, \varepsilon)$ with a Gaussian which represents the resolution $\bar{\rho}(\mathbf{r}, \varepsilon) \propto \int \rho(\mathbf{r}, \varepsilon') \exp[-(\varepsilon - \varepsilon')^2/W^2] d\varepsilon'$. A surface of constant density is then constructed according to $\bar{\rho}(x, y, z, \varepsilon) = C$, with C a constant. This construction implicitly gives the height $z(x, y)$ as a function of the position x, y which is then mapped linearly onto a gray scale. It mimics the presentation of STM images in the usual constant tunneling-current mode of operation. Qualitatively, the resulting images do not depend critically upon the choice of parameters W and C . We have used $W = 0.2$ eV and have set C to a value at which the maximum z is at ~ 2.5 Å above the highest atom.

The image of the LDOS of the highest occupied states associated with structure 1b is shown in Fig. 2(b). The π states formed from the ad-dimer and substrate-dimer dangling bonds dominate this filled state image. Note that dimers are distinctly buckled in this structure; the buckling angle of the ad-dimer is 11° , which is comparable with buckling angles of surface dimers on the clean surface [13]. At sufficiently high temperatures the dimers are not frozen into a single “up-down” configuration but will be found in the equivalent “down-up” configuration with equal probability. Flipping between these two configurations is observable in an *ab initio* molecular dynamics simulation [18]. In the LDOS image, averaged over the time sequence of configurations (trajectory), the ad-dimer as well as the substrate dimers have a more symmetric appearance, as shown in Fig. 2(c). A very interesting event occurs when we overheat our system [18]. A 0.4 psec trajectory of this simulation is shown in Fig. 2(d). Quenching to $T = 0$ at the end of this trajectory results in the LDOS shown in Fig. 2(f), which corresponds to the structure 1a, Fig. 2(e). The trajectory thus represents a rotation of the ad-dimer in which it starts from a configuration with the dimer axis oriented along the y axis and ends with it oriented along the x axis. The “reaction-path” in the sense of transition state theory is a direct one, without exchange between the ad-dimer and the surface atoms or even a breaking up of the surface dimers. In a previous paper we estimated that ~ 0.9 eV was an upper bound for the activation energy associated with this rotation [11].

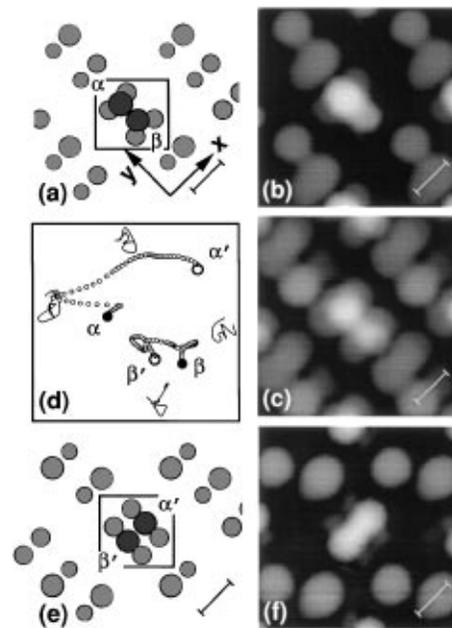


FIG. 2. (a) Geometric structure of the Si ad-dimer and the top layer of surface atoms. The size of the circles represents the height of the atoms, the atom marked α is 0.45 Å higher than the atom marked β . (b) An image of the local density of states (LDOS) $\bar{\rho}$ around the highest occupied states. The units of length indicated are 3.84 Å. (c) The LDOS averaged over a time trajectory. (d) Trajectories of the ad-dimer and some atoms in the top substrate layer 18, where the ad-dimer rotates from structure 1b (α, β) to structure 1a (α', β'). (e), (f) Geometric structure and LDOS after quenching to $T = 0$ K at the end of the simulation.

The possibility of observing the ad-dimer rotation at room temperature has been demonstrated quite convincingly by recent STM experiments [3–5].

Upon annealing, the formation of rows of ad-dimers, with the ad-dimers seemingly positioned between the substrate dimer rows, has been observed [5]. For an *isolated* ad-dimer on a perfect surface this position is energetically unfavorable as discussed above. However, for *rows* of ad-dimers the situation changes drastically. If we embed the structures of Fig. 1 in a $p(2 \times 4)$ surface unit cell, infinite ad-dimer rows are formed along the x axis, an example of which is shown in Fig. 3(a). The structures corresponding to infinite rows of configurations 1a–1d are optimized, and their relative energies are found to be 0.29, 0.27, 0.0, 0.34 eV, respectively. The cooperative effect of arranging ad-dimers in a row results in the structure shown in Fig. 3(a) being the lowest in energy. The ad-dimers have regular bond lengths of 2.35 Å and the substrate dimer bonds are stretched to 2.53 Å. For the isolated dimer of Fig. 1(c) the situation is reversed, illustrating the increased bonding in the ad-dimer row. The dimers in the ad-dimer row are buckled (buckling angle 11°). Dynamic buckling at higher temperature will make the ad-dimer rows

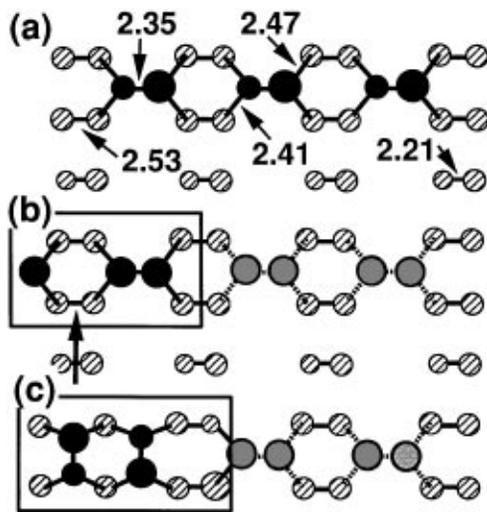


FIG. 3. (a) The structure of an infinite dilute ad-dimer row, with Si-Si bond lengths in Å. (b) The formation of a dilute ad-dimer row. The stable ad-trimer, enclosed by the black box, acts as a growth nucleus which promotes one-dimensional growth as indicated by the gray circles. (c) The formation of an epitaxial ad-dimer row. Insertion of an adatom, indicated by the arrow in (b), leads to the breaking of substrate dimer bonds and the formation of the stable epitaxial structure enclosed by the black box.

appear symmetric, corresponding to the experimental observations [5].

We propose the following mechanism for the formation of this structure. An isolated ad-dimer with the 1c structure is only metastable. However, it can be stabilized by an extra adatom. The adatom plus ad-dimer structure represented schematically in Fig. 3(b) has a 0.25 eV lower total energy than an isolated adatom at its global energy minimum position [10] plus an isolated ad-dimer with structure 1a or 1b. Ad-dimers with structure 1a or 1b do not bind an extra adatom, and therefore cannot act as growth nuclei. The stable ad-trimer acts as a nucleus promoting one-dimensional growth, as shown schematically in Fig. 3(b); a fourth adatom can form an ad-dimer with the third, etc. We have encountered such one-dimensional growth in our study of Al adsorption on Si(100) and called the mechanism, by analogy with polymer addition reactions, surface polymerization [19]. In contrast to Al, Si ad-dimers in these rows are not at positions which are most favorable for isolated dimers. Whereas a finite row of two Si ad-dimers is calculated to have no net binding energy with respect to two isolated ad-dimers in their minimum energy positions, rows of length $N \geq 3$ ad-dimers have a positive binding energy and thus represent a structure which is stable with respect to separation in individual ad-dimers.

There is a chemically intuitive reason for the stability of the ad-trimer as shown in Fig. 3(b). The LDOS of a single ad-dimer in structure 1c, at an energy corresponding to the highest occupied states, is dominated by the

features marked *D* in Fig. 4(b). These are dangling bonds on surface atoms created by breaking substrate dimer π bonds in order to form new bonds to the ad-dimer. These dangling bonds are reactive sites for the adsorption of adatoms (or ad-dimers), and adsorption at these positions results in an extra binding energy. Such dangling bond sites are not created in the ad-dimer structures 1a and 1b.

The identification of substrate dimers and ad-dimers in dilute rows from the STM images is relatively straightforward. In addition, features are observed which seem to correspond to single adatoms bonded to the end of an ad-dimer (row) [5,20]. According to the discussion in the previous paragraph, such structures are possible intermediates in the growth of a dilute dimer row. However, since such features are visible in the empty state images only [5], one has to be careful. Once again, the LDOS can be used to interpret these observations. The most simple symmetric structure of this kind, consisting of just one ad-dimer and two single adatoms, is shown in Fig. 4(c) [20]. Its energy is within 0.1 eV of that of a row of two ad-dimers, so it is relatively stable. The most prominent features in the LDOS of the highest occupied states, cf. Fig. 4(d), are the π states of the ad-dimer and the substrate dimers. In the LDOS of the lowest unoccupied states, cf. Fig. 4(e), the π^* states of the dimers and the p_z states of the two single adatoms are observed. We can rationalize these results in simple terms. The single adatoms are sp^2 -like hybridized; two sp^2 hybrids contribute to the bonding with the substrate, the third sp^2 hybrid is filled with two electrons (i.e., a lone pair), and the p_z state is empty. The lone pair has more *s* character than the π state of the ad-dimer (which has more p_z character) and is thus found at a lower energy. In the LDOS, the lone pair state is clearly visible at a lower energy, cf. Fig. 4(f). The lone pairs do not stick out of the surface such as the p_z states do, which makes adatoms almost “invisible” near an ad-dimer in a filled state STM image. One could, for instance, easily

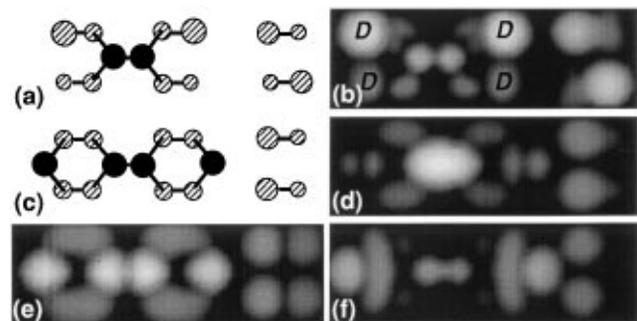


FIG. 4. (a),(b) The LDOS of the highest occupied states of the metastable ad-dimer 1c is dominated by dangling bonds on surface atoms, marked *D*, which are preferential adsorption sites for adatoms or ad-dimers. (c) Structure which corresponds to an ad-dimer plus two single adatoms. (d) The LDOS of the highest occupied states (at energy ϵ_{0c}) corresponding to this structure. (e) The LDOS of the lowest unoccupied states. (f) The LDOS at the energy $\epsilon_{0c} - 0.5$ eV.

misinterpret the filled state image of Fig. 4(d) as being that of an isolated dimer [3]; the single adatoms show up only in the empty state image, Fig. 4(e).

Epitaxial dimer rows are more stable than dilute dimer rows, so the latter can only be an intermediate step for epitaxial growth. Looking at the structure of a dilute ad-dimer row, cf. Fig. 3(a), we observe that the dimer bonds of substrate dimers bonded to the ad-dimers are stretched (2.53 Å), compared to those of adjacent “free” substrate dimers (2.21 Å). It can be expected that such stretched bonds will open more easily upon the arrival of an additional adatom or ad-dimer. Moreover, isolated adatoms or ad-dimers diffuse preferentially along the substrate dimer rows [1,10–12], and are thus likely to sample the stretched bond positions. An example of such a process is shown schematically in Figs. 3(b) and 3(c), where an extra adatom combines with an adatom at the end of a diluted dimer row. The opening of two substrate Si dimer bonds creates locally an epitaxial structure (which has a ~ 0.4 eV lower energy as compared to two diluted dimers). Such processes convert the diluted ad-dimer row to an epitaxial ad-dimer row, as observed recently by van Dam *et al.* [20]. Presumably, the insertion of adatoms or ad-dimers in a dilute ad-dimer row involves an activation barrier, which is high enough to make the latter (meta)stable at low temperature; at higher temperatures only epitaxial ad-dimer rows are observed [12]. Both the dilute and epitaxial ad-dimer rows promote one-dimensional growth in the direction of the ad-dimer row (i.e., the x axis), since reactive surface dangling bonds are found at the end of such rows.

The authors wish to thank A. van Dam *et al.* [20] and T. Yamasaki *et al.* [15] for discussing their results prior to publication.

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[16] Calculations based upon the empirical Stillinger-Weber (SW) potential predict that the ad-dimer structures 1c and 1d are more stable than the structures 1a and 1b, Ref. [3]. This potential is fitted to bulk Si properties, and it tends to describe the bonding of undercoordinated Si atoms such as those found on a surface poorly. Most noteworthy is its complete failure to describe the reconstruction and the energetics of adatoms on the Si(111) surface; see X.-P. Li *et al.*, Phys. Rev. B **38**, 3331 (1988); B. C. Bolding and H. C. Andersen, Phys. Rev. B **41**, 10568 (1990). For the Si(100) surface, the SW potential does not yield the inward relaxation of the surface, nor the buckling of the surface dimers [13,14].

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