Energetics and Dynamics of Si Ad-Dimers on Si(001)

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The energetics and dynamics of Si ad-dimers on Si(001) have been investigated by total-energy calculations and scanning tunneling microscopy. Several dimer configurations and a thermally activated rotational mode of the dimer on top of a dimer row are theoretically predicted and experimentally identified. The frequency of occurrence of the different dimer configurations suggests a likely pathway for monomer diffusion.

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The properties of the Si(001) surface and the dynamical interactions of Si adatoms on and with this surface have been the subject of extensive theoretical and experimental study. Recent scanning tunneling microscopy (STM) measurements and calculations have explored the adsorption, diffusion, and growth of Si atoms on Si(001) [1–7]. In spite of these efforts, many fundamental questions remain about even these simple processes. Among them are the identification of stable adsorption sites of Si atoms on Si(001)-(2×1) and the migration between sites. Calculations have predicted very different stable sites and various microscopic mechanisms for adatom motion [3–6,8,9], including a mechanism that preferentially causes adsorption of the atoms on top of dimer rows followed by very rapid diffusion parallel to the rows [5]. Experimentally, it has not been possible to confirm any of these mechanisms because measurements have been made only at temperatures too high to image adatoms [1,2,7]. Measurements of the diffusion coefficient of Si on Si(001) made by evaluating the density of Si islands that form for deposition at room temperature and above give only the rate averaged over all possible microscopic paths, but do show a considerable anisotropy of motion, preferentially along the dimer rows [7]. They also show that temperatures considerably below room temperature are necessary in order to possibly observe adatom motion directly. In one exception in which small Si cluster diffusion was studied by STM in "real time," it was impossible to determine unambiguously the size of the diffusing species [10].

In this Letter, we take the approach of looking at the properties of dimers on the surface, from which it becomes possible to deduce answers about the adatom adsorption site and about possible diffusion mechanisms of adatoms. The mobility of ad-dimers at room temperature or somewhat higher is low enough to image them readily. We identify the location as well as the orientation of ad-dimers. We observe and are able to determine, on the basis of theoretical calculations, the relative stabilities of several different dimer configurations, including the most stable configuration. We confirm experimentally a theoretically predicted thermally activated rotational mode of the dimer as it switches between two orthogonal and quasistable configurations located on top of a dimer row.

The implications of these combined theoretical and experimental results for the questions mentioned earlier are several fold. (i) Because isolated dimers are formed from monomers, we can extract information about the monomer diffusion pathways based on where two monomers are most likely to meet. (ii) Under reasonable assumptions, we can infer the likely stable adsorption sites of a monomer from the relative stabilities of the dimer configurations. (iii) A better understanding of the growth of larger islands obtains from an understanding of the nucleation process [1,2,7]. (iv) Our experimental results can be used to test the accuracy of various interaction potentials developed for silicon [3–6,8,9,11,12].

To facilitate the discussion we first introduce the notations and summarize the main results about *monomer* adsorption and diffusion obtained in two previous representative calculations, one [4] within the density functional theory, the other [5] using the empirical Stillinger-Weber (SW) potential [13]. In Fig. 1, the local minima in the potential-energy surface as mapped out by an adatom are marked by the small full squares within a (1×2) unit cell for the two calculations [4,5]. Besides the difference in the total number of local minima, in Fig. 1(a) the absolute minimum is at the M site, while in Fig. 1(b) it is at F. For migration between sites, essentially all calculations, using different interaction potentials, conclude that the faster direction of diffusion is parallel to the dimer rows [7], but very different diffusion pathways have been proposed [3–6,8,9]. Figure 1 contrasts two such proposed pathways for atom diffusion parallel to the dimer rows. Brocks, Kelly, and Car [4] proposed a zigzag path connecting two stable M sites, as indicated by the arrows in Fig. 1(a); the activation barrier along this path is 0.6 eV. Alternatively, Zhang, Lu, and Metiu [5] showed that, rather than finding the lowest-energy site, an arriving adatom finds it easier to give away its excess kinetic energy in some of the shallower local minima (e.g., at B) and adsorb there. A consequence of this population inversion in the earliest stages of adsorption is that an adatom will diffuse a long distance

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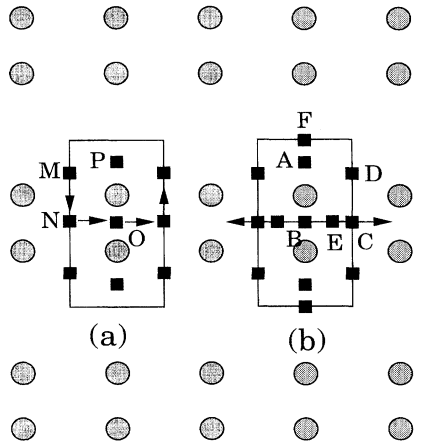


FIG. 1. Schematic diagrams of the interaction of a Si adatom with a Si(001) surface. The circles are the atoms in the top layer of the substrate; the squares indicate possible adsorption sites. In (a), from first-principles calculations, M is most stable; the preferable path for adatom diffusion is indicated by the arrows (Ref. [4]). In (b), from SW calculations, F is most stable; the double-ended arrows indicate that an adatom preferably travels on top of and parallel to the dimer row (Ref. [5]).

on top of and parallel to a dimer row before hopping into a stable F site. The maximum activation barrier along this "fast track" is only 0.3 eV, while the barrier preventing the atom from leaving this track and jumping into an F site is 0.7 eV. Once having reached F, an adatom can hop to a neighboring F site by overcoming a barrier of 0.9 eV.

We now present our theoretical results about *dimer* adsorption. As in Ref. [5], we use the SW potential to calculate the adsorption energies of an ad-dimer in several high-symmetry configurations; the results will be compared with similar calculations using different interaction potentials [11,12]. The substrate is modeled by an eight-layer slab containing a total of 1110 atoms. In calculating the total energy of a given configuration, the coordinates of 575 atoms contained in the inner region of the top five layers plus those of the two adatoms are fully relaxed. We have determined that the finite cluster size does not affect the relative energies.

The results are summarized in Fig. 2. For configurations of a dimer residing on top of a dimer row, the only energetically favorable site when the ad-dimer axis lies parallel to the dimer rows is as shown in Fig. 2(b) [11]: The adatoms reside on two neighboring B sites, as defined in Fig. 1(b), but are pulled somewhat towards each other by dimerization. In this configuration, the two dimers underneath the ad-dimer open. The height of the ad-dimer is 1.35 Å with respect to the substrate layer. A nearly degenerate adsorption site occurs when the ad-dimer axis is rotated by 90 deg. In this configuration, shown in Fig. 2(a), the ad-dimer resides halfway between two substrate dimers on D sites [Fig. 1(b)]; the total energy of the system is 0.06 eV higher than that of the configuration shown in Fig. 2(b). The height of the ad-dimer is 1.85 Å; this height increase occurs because the bonds of the two neighboring surface dimers are not broken. We have also estimated the rotational barrier from the configuration, Figs. 2(a) to 2(b), by displacing one of the ad-dimer atoms along a curve connecting its initial site D to a final site B, and leaving the other atom to adjust its position itself as the whole system relaxes to minimize its total energy. The rotational barrier thus mapped out is 0.76 eV.

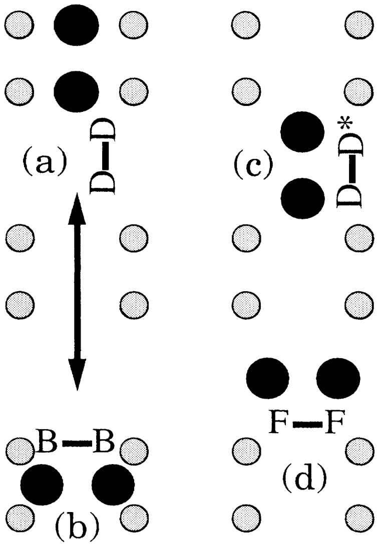


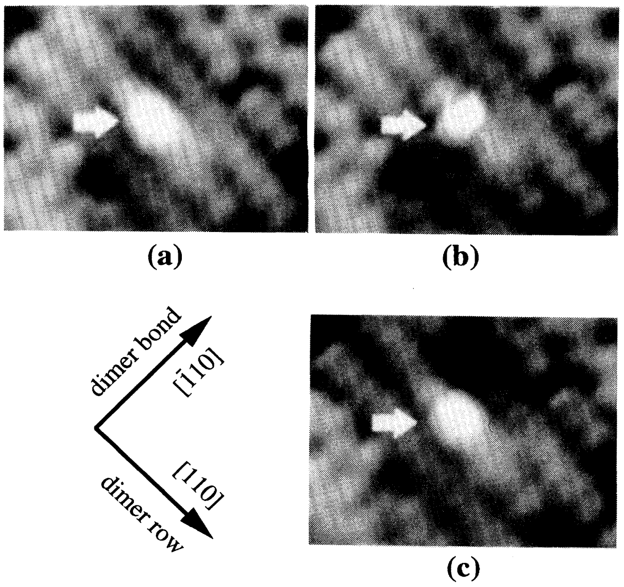
FIG. 2. Four different Si dimer adsorption configurations on Si(001). The filled circles are adatoms, and the shaded ones surface atoms. The letters correspond to the sites identified in Fig. 1(b). Calculations using the SW potential and STM studies show that (d) is the most stable, followed in order by (c), (b), and (a). (a) and (b) are reversibly convertible at room temperature.

Dimers residing between dimer rows are more stable that the ones residing on top. Both configurations, Figs. 2(c) and 2(d), are found, with Fig. 2(d) the most stable. In Fig. 2(c), the adatoms occupy D sites located on two adjacent dimer rows. The height of the ad-dimer is about 1.36 Å with respect to the surface layer. In Fig. 2(d), the adatoms reside on neighboring F sites. The height of the ad-dimer, 0.96 Å, is the lowest. The rotational barrier from Figs. 2(c) to 2(d) is 1.0 eV. The dimer adsorption energies follow the inequality chain: $E_{F\text{-}F} = -7.82$ eV $\ll E_{D\text{-}D^*} = -7.03$ eV $< E_{B\text{-}B} = -6.96$ eV $< E_{D\text{-}D} = -6.90$ eV, all measured with respect to the reference configuration in which the two adatoms are far from each other and well above the surface. Taking the configuration, Fig. 2(d), as the reference, we have $E_{2(\mathrm{d})} : E_{2(\mathrm{c})} : E_{2(\mathrm{b})} : E_{2(\mathrm{a})} = 0 : 0.78 : 0.86 : 0.92$ eV. We note that there is a close correspondence between the stable adsorption sites of monomers and dimers: The stable configuration for *dimer* adsorption [Fig. 2(d)] is that in which its two adatoms reside at the most stable *monomer* adsorption site [site *F* in Fig. 1(b)].

To perform the measurements we clean Si(001) in the usual manner [14]. After the sample cools to room temperature, about 0.01 monolayer (ML) of Si atoms is deposited. The sample is either transferred directly to the STM, or first annealed at 400 K. The images are taken at a negative sample bias of 2 V, with a constant tunneling current of 0.1 nA.

Figure 3 shows high-magnification images of dimers on the surface. Larger images show that most of the ad-dimers reside on top of the dimer rows, suggesting that the monomers that have created these dimers have traveled on top of a dimer row. Additional support of this point will be provided later. We can resolve two different elongations in the images of dimers on top of dimer rows: perpendicular to the substrate dimers [*B-B* dimers, Fig. 2(b)], and parallel to the surface dimers [*D-D* dimers, Fig. 2(a)]. The theoretically predicted height difference between these two configurations is not unambiguously reflected in the relative brightness of the images, because the electron distribution will differ for different dimer configurations.

It has been generally assumed that newly formed ad-dimers are oriented *perpendicular* to the substrate dimers [Figs. 2(b) and 2(d)], because that is their orientation in dimer-wide islands grown on the substrate [1,2,7]. The present results demonstrate that this orientation develops only later in the growth process. It was clear early on that initial growth mechanisms of Si on Si(001) were complex: The observation [13] of "diluted-dimer" ends of adsorbed dimer-wide islands demonstrated that two binding sites exist for dimers with the axis oriented perpendicular to the substrate dimers (*B-B* and *F-F* in Fig. 2). The predominant configuration shows a dimer in the *B-B* position, with the adjacent *F-F* position missing [15,16]. The observation of the *parallel* orientation is new. In addition, Fig. 3 demonstrates that an ad-dimer can oscillate between the two orthogonal orientations. The time separation between these images is 40 sec. The field of the tip appears not to be a dominant factor here, as frequent and infrequent scanning over the same dimer does not change the results significantly [17].



(a) (b) (c)

FIG. 3. STM images, taken after 0.01 ML of Si atoms have been deposited onto Si(001) at room temperature, with high magnification to show the behavior of an ad-dimer. (a)–(c) are each separated in time by 40 sec. The dimer indicated by the arrow rotates. In (a), its axis is perpendicular to the substrate dimers, a configuration shown in Fig. 2(b). In (b), the ad-dimer has rotated by 90 deg, as shown in Fig. 2(a). In (c), the ad-dimer has rotated back. Shown at the lower-left corner are the dimer-bond and dimer-row directions of the substrate.

The ratio $n_{D\text{-}D}/n_{B\text{-}B}$ remains approximately constant for hours at room temperature. It is therefore reasonable to assume that *local* thermal equilibrium has been reached between these two bonding configurations. Large-area counting yields a relative population of these two orientations $n_{D\text{-}D}/n_{B\text{-}B} \sim 1/(10 \pm 2)$. From this ratio, we estimate that the *B-B* dimer is more stable by 0.06 ± 0.01 eV. Neither, however, needs be the true equilibrium configuration, as they may be kinetically prevented from reaching more stable configurations.

To examine the possibility that kinetic limitations prevent dimers from reaching more stable configurations, we annealed the as-grown system to 400 K for times ranging from a few seconds to several minutes. Annealing increases the concentration of dimers lying between the dimer rows. For short times, many of the ad-dimers that have jumped into the trough are oriented parallel to the substrate dimers [Fig. 2(c)]; further annealing increases the population of ad-dimers in the stable configuration [Fig. 2(d)]. At an annealing time $t_a = 12$ sec, the population of dimers in the trough has increased from about 30% (right after deposition) to 50%; at $t_a = 60$ sec this population is 65%.

The experimental demonstration that the between-row dimer configurations are more stable reaffirms the point made earlier, namely, that monomers must have landed preferentially on top of the dimer rows and spent time traveling there before running into each other to dimerize. If they were mainly traveling between dimer rows, they would more likely form stable dimers in the trough at their first encounter.

In summary, we have investigated the properties of Si ad-dimers on Si(001). We are able to learn not only interesting properties of these dimers, but are also able to use these properties to deduce information on the behavior of monomers. We have demonstrated that Si ad-dimers on Si(001) exist in several configurations. Most of the ad-dimers are initially found on top of dimer rows as monomers are deposited onto the surface at room temperature. This observation forces us to conclude that monomers are preferentially adsorbed on top of dimer rows and that they spend a considerable part of their lifetime diffusing on top of dimer rows. Once they are formed on top of dimer rows, ad-dimers undergo rotations between two orthogonal and quasistable configurations. This rotational mode is believed to be thermally activated. The most stable dimer configuration (halfway between two dimer rows, with the ad-dimer axis parallel to the substrate dimer rows) is reached upon annealing, via another intermediate configuration. The nucleation process for Si on Si(001) is thus much more complex than has been anticipated.

Many of these observations have been predicted by calculations in this work using the SW potential. Whereas it would be unwise to expect this semiempirical potential to give accurate energies, the nature of kinetic mechanisms and the qualitative ordering of the energetic processes appear to be reliably predicted. In contrast, a recent first-principles calculation [11] gave an opposite energy ordering ($E_{2(\mathrm{a})} : E_{2(\mathrm{b})} : E_{2(\mathrm{c})} : E_{2(\mathrm{d})} = 0 : 0.1 : 0.5 : 1.8$ eV). In Ref. [11] the configuration, Fig. 2(d), is not even quasistable, while experimentally it clearly is. It is not clear why the first-principles calculation, which in principle should be more reliable, disagrees so severely with the experiments. We speculate that the much smaller clusters used in these calculations might be too small to closely model the ad-dimer or substrate system. Another calculation [12], using a modified SW potential, gave an energy ordering ($E_{2(\mathrm{d})} : E_{2(\mathrm{b})} : E_{2(\mathrm{c})} : E_{2(\mathrm{a})} = 0 : 0.76 : 1.44 : 1.68$ eV) that partially agrees with experiment; it also gave a difference $E_{2(\mathrm{a})} - E_{2(\mathrm{b})} = 0.9$ eV that is much too large. A more detailed comparison between the results of various different experiments is presented elsewhere [18].

The existence of several possible quasistable states for the stable nucleus is likely to be a more general phenomenon, especially on surfaces with low symmetry. A detailed investigation of the kinetic and energetic properties of dimers with STM will allow the testing of the accuracy of interactions potentials, and predictions about more complex systems. An example of the latter is the recent STM study of the thermal decomposition of disilane on Si(001) [19], in which H atoms coexisting on the surface might help to stabilize some of the ad-dimer configurations shown in Fig. 2. It should be possible, on the basis of the present results, to determine as well the influence of impurities on the nucleation and growth process in this and other systems.

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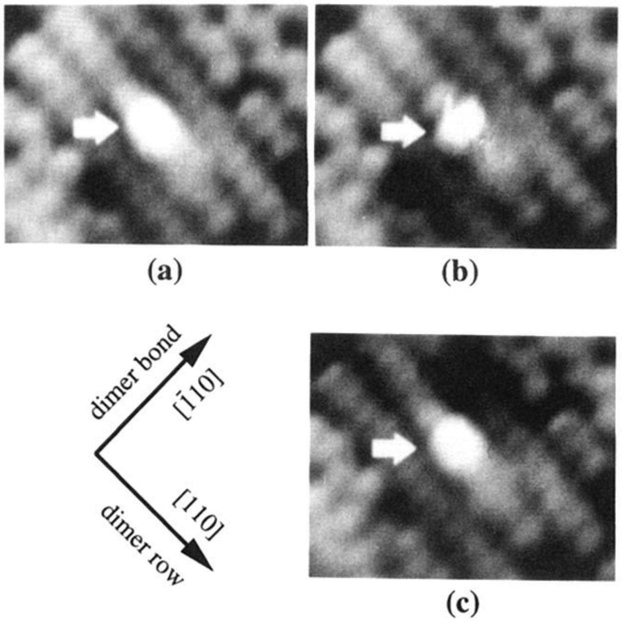

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