Evidence of Adsorbed Atom Pairing during Homoepitaxial Growth of Silicon

Robert A. Wolkow

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Canada K1A 0R6
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The early stages of silicon homoepitaxy on Si(100) are studied with low temperature scanning tunneling microscopy. Adsorbed atoms and epitaxial dimers are observed. Adsorbed atoms form previously unobserved pairs which couple via a substrate mediated interaction. Transient nonthermal atomic motion leads to the formation of atom pairs and epitaxial dimers. A paired atom acts as if constrained by a potential trough and exhibits a lower barrier to motion than an unpaired atom. Paired atoms are observed to coalesce into a normal, epitaxially oriented silicon dimer.

The epitaxial growth of silicon on Si(100) has been extensively and profitably studied using scanning tunneling microscopy (STM) [1]. These studies have all involved deposition of silicon atoms onto a Si(100) crystal held at room or an elevated temperature. The smallest features seen in these studies are epitaxially oriented dimers. A single adsorbed Si atom has a transient existence at room temperature, because it is sufficiently mobile to find another atom, a group of atoms, or a step edge, where it becomes permanently bound. As a result adsorbed silicon atoms are never observed in room temperature STM images. Because of this limitation, many fundamental questions have remained unanswered. The first of these involves the atom adsorption site. Though dealt with at various theoretical levels [2], an experimental determination is needed, since knowledge of this site is a prerequisite for understanding the epitaxial growth process. The processes that atoms enter into while moving toward the formation of the simplest epitaxial unit, the dimer, also need to be experimentally elucidated. In addition, it is of interest to determine the extent that nonthermal processes—dynamics that proceed as a result of the heat of adsorption and which terminate when that energy is dissipated—contribute to adsorbate distributions. These issues are addressed in this work.

The first low temperature STM study of Si adsorption on Si(100) is presented. At 160 K adsorbed silicon atoms are found to be immobilized and their adsorption sites are determined. Epitaxial dimers and unique paired adsorbed atoms are observed. The paired atoms, as distinct from atoms within an epitaxial dimer, do not share a chemical bond but are coupled via a substrate mediated interaction. A paired atom can hop to a new adsorption site toward or away from its partner, but constrained to a line at a right angle to the substrate dimer row direction. Since atoms cannot diffuse at the low temperature studied, it is apparent that some form of short-lived nonthermal atomic motion leads to the formation of paired atoms and epitaxial dimers. Atoms in the paired configuration are occasionally observed to coalesce to form epitaxial dimers, providing new insight

into epitaxial growth dynamics while also providing a direct view of the formation of a single chemical bond.

The cryogenic variable temperature STM used in this work has been described in detail elsewhere [3]. The ion/titanium sublimation pumped ultrahigh vacuum chamber has a base pressure $<1 \times 10^{-10}$ Torr. Arsenic doped, 10^{-3} Ω cm Si(100) wafers (Virginia Semiconductor) were resistively heated to 680 °C for approximately 8 h to degas the sample and holder before a quick flash at 1200 °C. Tips were formed from electrochemically etched tungsten. The silicon source was a resistively heated 1 Ω cm crystal. At 1200 °C the source deposits approximately 1 ML per 100 s onto the crystal under study. Doses were on the order of several seconds and were controlled by opening and closing a shutter. During exposure the chamber pressure remained in the low 10^{-10} Torr range. Deposition onto a room temperature substrate resulted in reproduction of previously published results [1]—dimers were observed, atoms were not. No evidence is found that the very small concentration of dopant and impurity atoms in the source affect the results reported here. The defect density on the surface before and after silicon deposition was ~0.5%.

Figure 1 shows a silicon surface that was held at 160 K during deposition and while imaging. In this grey scale depiction, shades of grey ranging from black to white correspond to a tip displacement normal to the surface of approximately 2 Å. The long structures running up the length of the image are rows of silicon dimers. A step up to another terrace is visible (the row direction rotates by 90° on traversing a single atomic step). The inset provides a schematic view of the surface. The larger of the white protrusions in Fig. 1 are epitaxially oriented silicon dimers [4]. The smaller protrusions are adsorbed silicon atoms. The deposited silicon coverage is 2% (determined from images). 40% of the atoms appear as dimers, the remainder as atoms. The dimer and atom features were absent before silicon deposition.

Figure 1 shows examples of individual atoms, and also, silicon atoms which appear to be paired [5]. By laying a grid over the image, the position of the adsorbates can be
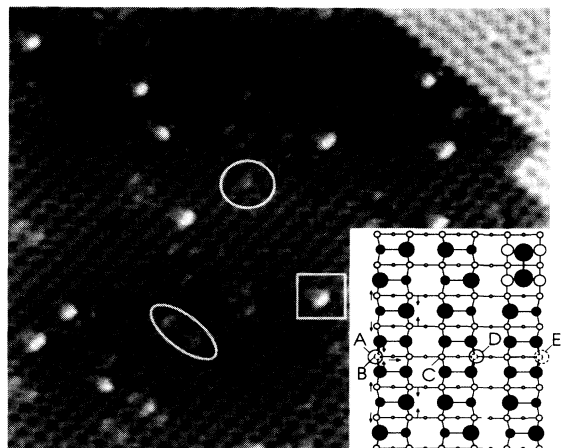
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FIG. 1.   160 K image of Si(100) recorded at -2 V (crystal) bias and 0.1 nA. The circle encloses a single adsorbed silicon atom. The square encloses a dimer, and the ellipse a pair of atoms. The inset shows adsorbed atoms (large open circles) and shaded substrate dimer atoms. Buckling of dimers is indicated by large (higher) and small (lower) circles. An epitaxial dimer is shown at the top of the right row. Dimer spacing in a row is 3.84 Å, row to row spacing is 7.68 Å.

readily identified as being just off the end of two adjacent dimers, in agreement with theory [2]. The bonding geometry is indicated schematically in the Fig. 1 inset. The paired atoms show several distinctive characteristics. (1) The atoms lie along a line that is at a right angle to the substrate dimer row direction, (2) the paired atoms can exhibit jumps to an adjacent row, (3) when separated by one or more rows, intervening rows show an interruption in their buckling pattern, and (4) a ridge is apparent between the atoms. These points will be expanded upon below. It will be helpful to first briefly describe the nature of the Si(100) surface [6].

The reconstruction of the Si(100) surface involves the formation of dimers. Conceptually, the dimers form as two bulk terminated surface atoms, with two dangling bonds each, tilt together to form a shared bond, leaving each atom with one dangling bond. The dimers line up in rows, with the bonds parallel. Dimers have a preference for a buckled geometry with one atom rising up and the other lowering [6]. Dimers in a row are coupled in an anticorrelated manner, giving rise to a zigzag appearance along rows of buckled dimers. The anticorrelated pattern is never violated unless interrupted by an adsorbate or a defect. Dimers will spontaneously buckle below approximately 200 K, while at room temperature the dimers freely flip between one buckled configuration and the other, leading to a symmetric appearance in STM images. At room or at low temperature, various defects and adsorbates can act to pin adjacent dimers into a buckled state. Frustrated dimers, receiving out

of phase buckling influences from surrounding defects or adsorbates, may fail to appear buckled at low temperature. Dimer buckling is important in this study as it helps to identify the adsorption sites of atoms, in much the same way as ripples in a pond indicate where a pebble fell. In particular, since adsorbed silicon atoms are positioned between two surface dimers, the buckling pattern extending along the row in one direction is out of phase with buckling in the other direction. This is shown schematically in the Fig. 1 inset.

On occasion one of the atoms within a pair jumps to the next row (either toward or away from its partner). Figures 2(a) and 2(b) provide an example of an atom jumping. Atoms have been observed to move as far as two rows apart. Motion is confined to the line defined by the paired atoms. This constrained motion taken together with the initial placement of the atoms in pairs indicates that these atoms are coupled or interacting in some way. Since the atoms are too far apart (8 Å or more) to share a chemical bond, there must be a substrate mediated interaction. Further indication of a through-substrate interaction is seen in the buckling pattern of dimer rows that intervene between paired atoms. As shown in Fig. 2(c) the buckling pattern in the row marked with an arrow shows a phase break even though no atom is adsorbed there. Furthermore, a slight ridge exists between paired atoms suggesting that pairs of dimers in intervening rows are held in an aligned configuration that gives rise to this feature. Evidently, the combined effect of two adsorbed atoms sufficiently alters the surface to create a potential "trough" that acts to trap the atoms.

A comment can be made at this point regarding silicon atom diffusion. It is commonly thought that diffusion on Si(100) is anisotropic, specifically (single atom) motion along the dimer row direction involves a smaller barrier than motion across dimer rows [7]. The motion observed in this work involving across row motion of paired atoms is a third and unique avenue. Whether the paired atoms are moving thermally or with some form of assistance from the tip is unclear at this point. It is reasonable to assume, however, that the motion observed, whether thermal or assisted, involves overcoming the smallest barrier. Since single atom motion is not observed, it may be concluded that motion of atoms within a pair involves a smaller barrier.

Some estimates of the energetics of the various processes observed can be made. Since unpaired atoms are not observed to move, a lower limit on the barrier to diffusion can be made. The maximum observation time is ~ 3000 s. Assuming a preexponential of 10^{13} s^{-1}, the barrier to diffusion is at least 0.56 eV. We find 10% to 20% of paired atoms exhibit a jump in an observation time of ~ 500 s indicating a barrier of 0.52 ± 0.01 eV.

It is clear that no thermally driven diffusion is occurring at 160 K that could lead to the formation of atom pairs or epitaxially oriented dimers [8]. It is at first tempt-
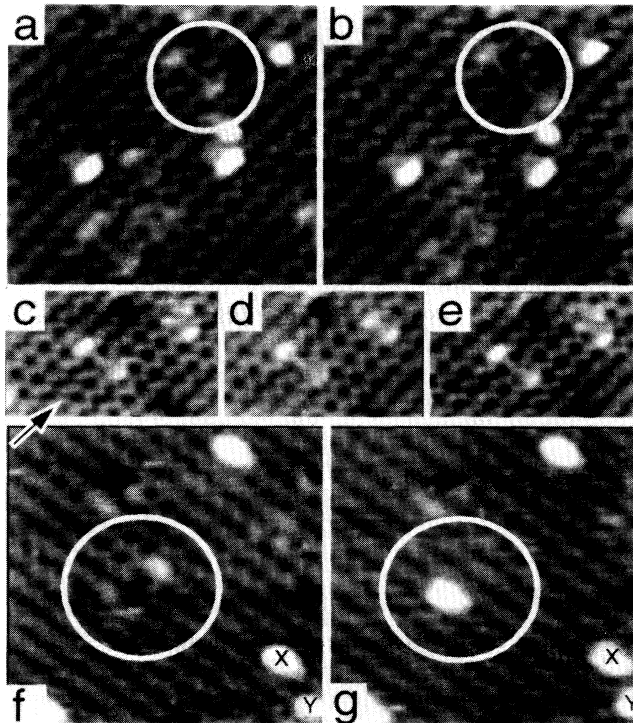
FIG. 2. Images (a) and (b) are of the same area and were recorded in sequence. The circles in (a) and (b) highlight a pair of atoms where one atom has hopped to the next row. The arrow in image (c) indicates a row that does not contain an adsorbed atom but nevertheless shows a phase break in the buckling pattern. Images (c), (d), and (e) show two pairs of atoms. The lower left pair does not change through this sequence. The left atom of the upper right pair jumps from the blurred, to the distinct, and back to the blurred state. Images (f) and (g) show a pair of atoms converting to an epitaxial dimer. Approximately 100 s separates successive scans.

ing to assume that predominantly dimers are produced by the silicon source and that these adsorb intact to form epitaxial dimers and in some cases fragment to leave closely spaced atom pairs. Conventional wisdom among growers [who use molecular beam epitaxy (MBE)], however, holds that a thermal silicon source produces only atoms. Analysis of a source similar to the one used here demonstrated an output of approximately 98% atoms [9]. This fact, and the observation of adsorbed single atoms with no obvious partner, force the conclusion that atoms, not dimers, are impinging upon the surface. The observation of atom pairs and epitaxial dimers, therefore, suggests that some form of transient atomic motion is acting.

An incoming atom from a 1200 °C source has $\sim$0.1 eV kinetic energy. When the atom bonds to the surface it suddenly has one, or more likely two, bonds to the surface with an energy of $\sim$4 eV. This very hot atom, probably within a small number of vibrational periods, pumps energy into the surface until thermal equilibrium

is achieved. But until it cools off, the atom can easily overcome the barrier to diffusion (thought to be $\sim$0.7 eV [7]), and it will hop across the surface. How long this nonthermal mobility lasts and how far an adsorbate might travel is not well known. The formation of dimers and paired atoms at 160 K implies that the area explored by an incoming atom is quite substantial, and that at the coverage studied an atom has a good chance of encountering another adsorbed atom and forming a dimer or an atom pair. An order of magnitude estimate of the distance an atom travels taken from the mean spacing between adsorbates is $\sim$30 Å. In future work we will endeavor to extract a more accurate number with the aid of an appropriate model.

In recent years there have been several indications of transient nonthermal mobility of adsorbates in MBE [10], field ion microscope [11], and diffraction spot profile experiments [12], but the idea remains controversial. For many years it has been generally accepted that condensation at low temperature was a relatively straightforward event, leaving atoms essentially at their point of impact [13]. A recent theoretical model considering Si deposition on Si(100) concluded that crystallization was facilitated by transient atomic motion, not of the incoming atom, but of relatively distant atoms, as the impact energy was transmitted through the lattice by a rapid chain of events [14]. We note that the present results are consistent with transient adsorbate motion, but we must also allow for the possibility that adsorbate insertion occurs near the point of impact and is rapidly followed by displacement of another atom some distance away.

In addition to hops between rows, atoms occasionally take on a less obvious, smeared out appearance. In time ($\sim$several minutes), atoms in this state switch back to the more distinct state. An example of this behavior is shown in Figs. 2(c)–2(e). When this change occurs, the atom is evidently switching to another adsorption state on the surface. In the theoretical work by Brocks and Kelly [2], various adsorption sites, in addition to the global minimum, are identified. Some of these sites are separated by small lateral shifts and by potential barriers on the order of a few tenths of an eV. It is assumed that thermally, or perhaps with the aid of the tip, the atom occasionally populates one of these higher lying states, taking on a different electronic structure and, therefore, a different appearance in the STM image. A variation on this blurred atom effect occurs when the paired atoms are two rows apart. In that case a region in the intervening row between the atoms takes on a dark appearance.

One further motion of the paired silicon atoms remains to be discussed. As shown in Figs. 2(f) and 2(g), the atom pairs are occasionally observed to coalesce, forming a chemically bound, epitaxially oriented dimer. Once formed, these dimers are static, no further changes are observed. In the example shown, and in every case observed, one of the two atoms is in the blurred looking

state described in the preceding paragraph. Interesting details emerge upon careful examination of the images taken before and after dimer formation. The preexisting dimers labeled x and y are immobile and common to both images and serve as convenient reference points. The distinct looking atom of the original pair is located in the row containing dimer x in Fig. 2(f). Study of the same row in Fig. 2(g) reveals that that atom is no longer present after the dimer has formed. Similarly, the darkened region in the row shared by dimer y is not evident in Fig. 2(g). The new dimer sits in the position previously occupied by the blurred looking atom. These observations satisfy the concern that material is conserved, and that the new dimers are not somehow dropped from the tip.

To end this discussion we propose a simple model, based upon adsorbate induced strain and associated displacements that account for the appearance of paired silicon atoms. Referring to the Fig. 1 inset, the atoms that bond to adsorbed atom A will be pulled together slightly, as approximately indicated by the arrows. The second layer atom B is in turn pushed down. Following the diagram, this sets up a chain of subtle displacements (third layer atoms down, second layer atoms up) that ultimately lead to an upward force on the second layer atom labeled C. In a theoretical treatment of Ge adsorption on Si(100) a very similar strain induced effect was predicted to interrupt the buckling pattern in an adjacent row [15]. Since displacements in second layer atoms are integrally involved in accommodating anticorrelated buckled dimers (see figure), displacement of atom C hinders the alternating buckling pattern and aids the dimers bonded to atom C in attaining a parallel configuration. The strain associated with adsorbate A is therefore supportive of atom pairing. Adsorption at site D forces attached dimers into a parallel configuration and also induces up and down motions of second and third layer atoms, respectively. Consider now adsorption at position E (with site D vacant), the adsorbed atoms cooperate to alter the environment around the pair of central dimers, leading to the observed break in the buckling pattern in that intervening row.

Continuous epitaxial growth cannot proceed at 160 K. This low temperature study, however, has revealed a variety of new phenomena that are integral parts of the growth process. The paired silicon atoms display substrate mediated coupling, which we assert arises as a result of adsorbate induced strain that acts to capture and constrain atoms in a particular region of the surface. This effect may have important consequences during epitaxial growth, since it suggests that atoms need not approach directly along a common line to interact, rather, the atoms have a large effective capture cross section, allowing interaction between atoms separated by several substrate dimer rows [16]. The appearance of paired atoms and epitaxially oriented dimers is consistent with substantial transient atomic motion. The need for further modeling exploring all aspects of paired atoms is clear. It will

be particularly interesting to determine whether motion of adsorbed atoms involves hopping, or if an insertion and displacement process is acting [17]. Finally, the coalescing of paired atoms to form an epitaxial dimer provides a direct view of the formation of an individual chemical bond while providing new insight into the dynamics underlying this important growth process.

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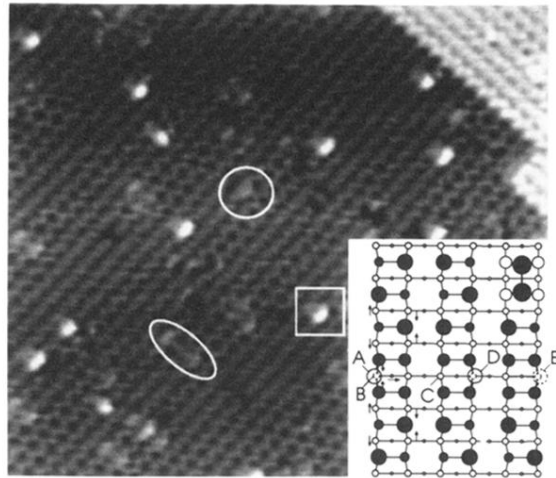[17] G. L. Kellog and P. J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990).

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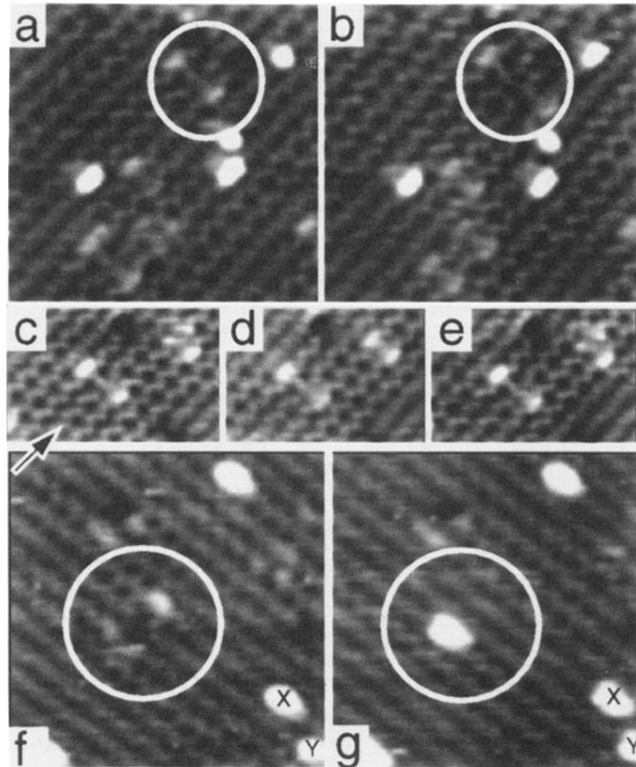
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