Modification of Si(100) Substrate Bonding by Adsorbed Ge or Si Dimer Islands

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High-resolution scanning tunneling microscopy studies of the Si(100)-(2 × 1) surface show a heretofore unrecognized distortion of the substrate structure when islands form during the initial stage of growth of either Si or Ge. The distortion, reflecting the influence of strain, extends at least three dimers away from the adsorption sites. We present a realistic structural model. [S0031-9007(98)07080-X]

It is well established that structural modifications at surfaces occur to allow the surface to reach its thermodynamic equilibrium condition by arranging the atoms so as to minimize the surface free energy. Such modifications, of which surface reconstruction and relaxation are the best known, are associated with reduction in both chemical bond energy and strain energy. Structural modifications can also occur more locally, e.g., at steps [1,2] or at vacancies [3,4].

If surface structural modifications can occur at steps and at vacancies, it is obvious that they should also be found locally in association with adatoms or small growth structures, as the chemical bond arrangement is modified through the adsorption. In particular, one might expect significant adsorbate-induced structural modifications on semiconductor surfaces because of the highly directional bonding. Yet the extent of relaxation associated with the initial stages of adsorption is not well known [5,6].

The nature of these structure modifications is most fully explored on the (100) surface of silicon. This surface has been extensively investigated because of its technological importance and because it represents an ideal model for semiconductor epitaxy [1]. Through use of the scanning tunneling microscope (STM), the generalized statistics of epitaxial island formation and growth roughening have been well established. On a local scale, the dimer structure of Si(100) has long been known [2,3,7], and STM has shown that atomic defects cause local dimer tilting ("buckling") [3]. The behavior of adsorbates on Si has recently also been investigated, and an influence on substrate dimer buckling has been demonstrated [8,9]. STM experiments so far, however, have not been able to detect an influence on the substrate structure by adsorbed small islands.

In this Letter, we describe a heretofore unrecognized modification of the substrate structure of Si(100) in the vicinity of a diluted ad-dimer island. We are able to do so with careful measurements at biases that are conventionally inaccessible. Our approach provides a significant enhancement of STM sensitivity to the surface states, offering the first view of the substrate strain field induced by ad-dimers. The measurements allow us to construct a more realistic structural model of the region in the vicinity of an ad-dimer island by including the local substrate modification.

The experiments were carried out in an ultrahigh vacuum STM with a base pressure below 1×10^{-10} Torr. The clean Si(100)-(2 × 1) surface was prepared in the conventional manner by degassing a wafer at 970 K, flashing at 1470 K for ~1 min, and slowly cooling. Ge was deposited from a resistively heated W wire basket with an intervening shutter to a typical coverage of ~0.01 ML (monolayer). The substrate temperature remained below 330 K during deposition. Si was deposited in a similar manner but using a resistively heated Si wafer. When Ge was deposited, substrates were used only once, and were imaged by STM beforehand to ensure a high-quality 2 × 1 surface with point defect density <0.5%.

When ~0.01 ML of Ge is deposited onto a Si(100)-(2 × 1) surface near room temperature, diluted ad-dimer islands are often found [9] with a structure similar to that observed in submonolayer Si growth [10,11]. The islands are perpendicular to the substrate dimer rows and consist of ad-dimers in adjoining substrate troughs [10] with their dimer bonds parallel to that of substrate dimers [11]. Figure 1 shows a STM image of such a diluted-dimer island, but with one major difference: Whereas conventionally filled-state images and high-bias empty-state images of such diluted-dimer islands are shown [9–11], this one is an empty-state image taken at a very low sample bias, +0.8 V. Such images are achievable only with a very sharp tip and a very-low-noise environment. For reasons described briefly below and detailed elsewhere [12] we are able to see a striking new feature: a modification of structure of the substrate dimers on each side of the diluted ad-dimer island. This modification extends out for at least three dimers.

The locations of the four substrate dimers nearest to the diluted-dimer island are marked with lines (Fig. 1). The substrate dimers (line 1) directly connected to the ad-dimers are obscured by the ad-dimers and not observable in the image. However, the second-nearest substrate dimers (line 2) display a well-defined deep minimum at the center of each dimer bond. The third-nearest dimers (line 3) have a weak but still visible minimum at the dimer-bond centers.
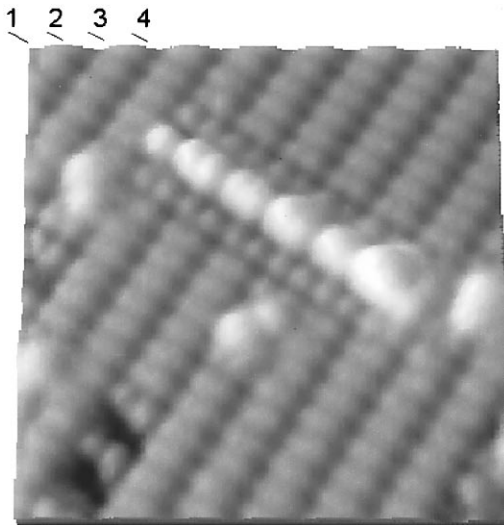
FIG. 1. Low-bias empty-state image of a diluted Ge ad-dimer island. The substrate structure in the vicinity of the island is modified. Sample bias: +0.8 V. Image size: 75 Å × 75 Å.

FIG. 2. Top view of substrate dimer rows. The circle size represents the height of Si atoms and the dashed frame shows bulk (1×1) unit cells. (a) Statically buckled Si dimers. (b) Dimer row with dimer 1 pinned into a symmetric configuration. Arrows indicate directions for restoration of the displacements of the second-layer substrate atoms due to the "debuckling" effect.

The fourth-nearest dimers (line 4) are essentially the same as the dimers far away from the island, which appear as "beans." We will demonstrate here that the strain induced in the substrate by the diluted ad-dimer island causes a pinned symmetric-dimer structure in the substrate near the island. As strain falls off away from the island, a gradual transition from a pinned symmetric-dimer structure to the normal dimer structure occurs. We provide, in the end, a structural model.

To substantiate our claim and provide a more detailed explanation of the results, we first briefly review the structure of the Si(100) surface. The (2×1) reconstruction of clean Si(100) is formed with rows of tilted ("intrinsically buckled") dimers [3,7]. The two atoms of the dimer are positioned up and down relative to the surface plane. The dimer buckling is accompanied by charge transfer from the lower atom to the upper atom and a lateral displacement of a dimer from the center of the bulk (1×1) unit cell [7], i.e., from the dimer row axis. If these buckled dimers are "frozen," Fig. 2(a), the upper atom of a dimer pulls the second-layer atoms closer together while the lower atom of the dimer pushes the second-layer atoms apart, causing adjacent dimers to buckle in the opposite direction to accommodate the distortion [3,13]. Away from defects there is no intrinsic preference for one or the other atom in a dimer to be "up" or "down." At room temperature, the thermal energy is sufficient for dimers to oscillate between the two choices, which make them appear symmetric in a typical filled-state STM image [2,3].

In a recent study [12] we have shown that low-bias empty-state imaging emphasizes the dangling-bond state, i.e., the antibonding $\pi(\pi^*)$ state, and that the intrinsic buckled dimers [Fig. 2(a)] appear as beans, just like the beans in filled-state images, but for a reason that appears
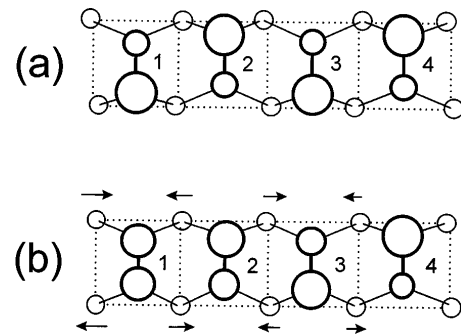
not to have been realized. Because the π^* state has a node in the middle of the dimer bond [7], any static Si dimer would in principle appear as two atomic protrusions in the image (depending on the orientation of the dimers, the two protrusions are not necessarily identical). In a buckled dimer, the node is shifted because the charge transfer leads to a polarized π^* state and because the dimer center of gravity is displaced. Oscillation of buckled dimers at room temperature shifts the node back and forth and smears it out, leading to the "bean-shaped" dimer in the empty-state images [12] far from the adsorbed island. Obviously, the bigger the buckling angle, the larger the shift of the π^* node, and hence the stronger the smearing-out effect when the dimer oscillates.

A true untilted ("symmetric") dimer will have a well-defined node and have a clear charge density minimum at the center of the dimer bond [7,14]. A well-defined minimum should also be observable for dynamically buckling dimers if they are more symmetric than the intrinsically buckled dimers; i.e., the π^* node is not shifted so much as to be totally smeared out. Room temperature imaging of such a dimer should in principle give two equal tunneling protrusions. The deeper the minimum is between these protrusions, the smaller is the buckling angle. These identifications are based on our new understanding of very-low-bias empty-state images of the substrate [12].

Figure 2(b) shows schematically the positions of atoms on the substrate in the vicinity of the adatom island, based on the view expressed in the last paragraph. We suggest, therefore, that the substrate dimers in lines 2 and 3 in Fig. 1 are in configurations that are more symmetric than those of intrinsically buckled dimers. Because the ad-dimers lie in substrate troughs, their bonding to substrate atoms would stretch the substrate dimers directly connected to them, and should also disturb the buckling of those substrate dimers. Qualitatively, as shown in Fig. 2(b), if the ad-dimer island causes dimer 1 (adjacent to the adatom island but not

visible in the image shown in Fig. 1) to be pinned into a symmetric configuration, the corresponding second-layer substrate atoms move in directions [arrows, Fig. 2(b)] that are against their original distortions [Fig. 2(a)]. Dimer 2 in line 2 (Figs. 1 or 2) will feel this strain and become less buckled. The strain field decays with the distance, and is felt at least 3 dimers away from the island along the substrate dimer rows. One could argue that, for dimers in lines 2 and 3 in Fig. 1, the bond length rather than the buckling changes. However, assuming that the distance between the two apparent protrusions for a dimer in line 2 reflects the bond length, its value, 3.5 Å, is unreasonably large for a dimer bond.

We have confirmed the above qualitative model of substrate dimer "debuckling" near Ge ad-dimer islands by first-principles pseudopotential total-energy calculations. We use a (4×8) surface supercell of a slab consisting of 8 layers of Si atoms, plus a 12 Å thick vacuum layer. A plane-wave cutoff of 11 Ryd is used, and the Brillouin zone is sampled with one special k point at Γ. An infinite Ge diluted-dimer island was added onto a predetermined $c(4 \times 2)$ substrate surface. All atomic positions (including adatoms) are optimized except the bottom 3 layers, which are fixed at the bulk positions. Atomic forces are minimized to better than 0.03 eV/Å. Because of the "debuckling" range seen in the STM image, a unit cell containing 8 dimers along a dimer row is the minimum requirement. The high anisotropy of the strain field justifies the use of a diluted-dimer island with infinite length to reduce computational demand.

Figure 3 shows the optimized atomic structure. Figure 3(a) is a side-projection view of the Ge adatoms and the top-layer Si dimers, which highlights the difference in height between the two atoms in the dimer as one moves away from the ad-dimer island. Figures 3(b) and 3(c) show the side and top views of the calculated supercell. The pinning of buckled dimers can best be seen in Figs. 3(a) and 3(b). The substrate dimers directly bonded to the diluted ad-dimers are calculated to be almost completely unbuckled, with a buckling angle of less than 1°. Moving away from the ad-dimer, the buckling angle (and hence height differences of the two atoms in the dimer) increases, with values of 0.9°, 13.6°, 15°, and 18.4° for dimers 1, 2, 3, and 4, respectively. The atomic configuration of dimer 4 is basically the same as the dimers in a clean surface. The bond lengths of dimers 2, 3, and 4 are about 2.30 Å, the same as in a clean surface, while the bond length of dimer 1 is stretched to 2.44 Å. The Ge ad-dimers have bond length of 2.67 Å and are virtually unbuckled. The ad-dimer-induced strain is relaxed primarily by bond rotation, reflecting the fact that it costs less strain energy to change bond angle than bond length. As expected, the unbuckling or partial unbuckling of substrate dimers near the ad-dimer island is accompanied by restoration of the lateral displacements of the second-layer substrate atoms closer to their bulk values as shown in Figs. 3(b) and 3(c).
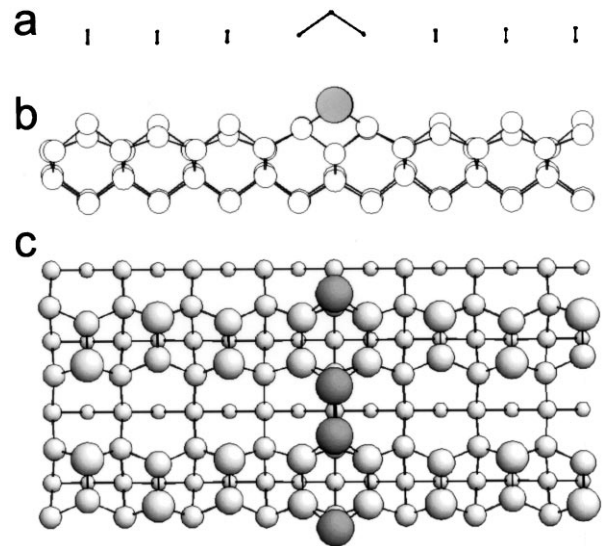

FIG. 3. Calculated atomic positions in the vicinity of an ad-dimer island: (a) side-projection view of Ge adatoms and the top layer of Si atoms; (b) side and (c) top views of Ge and the outermost four Si layers of atoms in the calculation supercell. As one moves closer to the ad-dimer, the decrease in the height difference between two atoms of a substrate dimer in the first substrate layer is better shown in (a), and the decrease of lateral splitting of two atoms of a substrate dimer in the second layer in (b). In (c) the height is indicated by size.

To alleviate the reader's concern that the STM image (Fig. 1) may be an artifact of the experiment, we present in Fig. 4 a series of images at different biases. They clearly show the progression from the conventional empty-state image to our low-bias empty-state image. As the bias is reduced, the substrate dimers generate a series of different images that reflect the changing view of the electron density, as detailed elsewhere [12], and the monomer and ad-dimers become better resolved. The effect is completely reproducible. At conventional biases, the modified structure is not observable because the imaging is not sensitive to the surface states.

Our results provide a more realistic model of the modification of substrate structure by diluted-dimer islands than has been previously considered [15,16]. Our results suggest an influence on further growth. In view of a recent study that the buckling of substrate dimers can have substantial effects on adatom binding energy and diffusion barriers [17] and, as monomers and ad-dimers approaching a diluted-dimer island from its sides will inevitably interact first with the partially unbuckled substrate dimers before they can react with the island, the debuckling status in the modified substrate may play an important role in the conversion of the diluted islands into epitaxial islands.

We have observed modification of the substrate structure similar to what we have described in Fig. 1 for both Si and Ge growth on Si(100) and for both diluted ad-dimer islands and dense (epitaxial) ad-dimer islands. A similar strain effect may also exist in the vicinity of missing-dimer
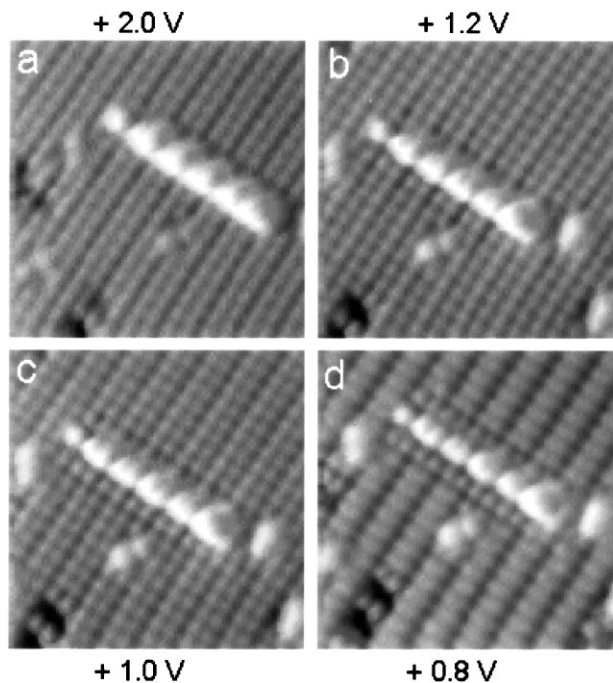
FIG. 4. Empty-state images of a diluted Ge ad-dimer island on Si(100) under different sample biases: (a) +2 V, (b) +1.2 V, (c) +1.0 V, (d) +0.8 V. The ad-dimers lie in the substrate troughs. A monomer is attached at the left end (Refs. [11] and [15]). (a) Shows the conventional high-bias image for which the substrate dimers show no modification near the ad-dimer island. (d) The same as Fig. 1. Image size: 75 Å × 75 Å.

defects (lower-left part of the image in Fig. 1). Substrate dimers close to such defects show well-defined deep minima. It is plausible to conclude that a debuckling effect exists in a more general way. It is well known that atomic defects (e.g., a step edge or a c-type vacancy) that are situated *asymmetrically* with respect to a substrate dimer row can either induce or stabilize buckling of local dimers [2,3]. The debuckling effects we observe show the oppo-

site behavior: Wherever atomic defects (either vacancies or adsorption species) are situated *symmetrically* with respect to a substrate dimer row, the substrate dimers near the defects are unbuckled or less buckled than the intrinsic buckled ones.

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