Dimer Pairing on the C-Alloyed Si(001) Surface

O. Leifeld,[1,2] D. Grützmacher,[2] B. Müller,[1] K. Kern,[1] Efthimios Kaxiras,[3,*] and P. C. Kelires[3]
[1]*Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[2]*Micro- and Nanostructures Laboratory, Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland*
[3]*Physics Department, University of Crete, P.O. Box 2208, 710 03 Heraclion, Crete, Greece*
(Received 29 June 1998)

The initial stages of carbon alloying into the Si(001) surface are studied by scanning tunneling microscopy (STM) and density functional theory. Carbon increases the surface roughness compared to the clean surface and induces a $c(4 \times 4)$ reconstruction. To explain experimental observations, we propose a novel surface reconstruction model that involves pairing of Si dimers mediated by the presence of a complex of a C dimer and four nearest neighbor subsurface C atoms. The model is backed by total energy and thermal stability simulations. Its calculated surface charge density agrees well with the filled state STM images. [S0031-9007(98)08302-1]

PACS numbers: 68.35.Dv, 61.16.Ch, 68.35.Bs, 71.15.Nc

Epitaxial alloys of column IV elements grown on Si vastly extend the range of electronic properties that can be obtained using Si alone. In particular, the ternary SiGeC alloy system has attracted much attention recently, as the band gap and the strain can be controlled independently [1]. Besides the possibilities in strain and band gap engineering, the incorporation of carbon also provides novel routes to control the self-organized growth of quantum dots. Recently it has been demonstrated that a submonolayer of carbon predeposited on Si(001) increases the density (reduces the size) of Ge quantum dots and substantially enhances their luminescence [2,3]. So far very little is known about C incorporation on Si substrates, which is very difficult due to the very large lattice mismatch between the two bulk materials (~35%). This fact makes detailed studies of the structure and properties of the C/Si(001) system of particular interest, from a fundamental point of view.

In the present Letter we report a combined experimental and theoretical study of the initial stages of C deposition on Si(001) substrates. We discovered that carbon causes an unusual $c(4 \times 4)$ reconstruction. We propose a structural model backed by detailed density functional theory (DFT) calculations that can account for all the observed experimental scanning tunneling microscopy (STM) results.

In the experiment four-inch Si(001) wafers are processed in a Si molecular beam epitaxy system equipped with an *e*-beam evaporator for Si and a sublimation source for carbon, the latter consisting of a dc heated graphite filament. Prior to C deposition, a 200 nm thick Si buffer is grown at a substrate temperature of 550 °C. 0.05 to 0.11 monolayers (ML) carbon are then evaporated at a growth rate of 3.3×10^{11} atoms/s at 550 °C, calibrated by secondary ion mass spectroscopy. After C deposition the samples are cooled to room temperature and transferred under ultrahigh vacuum to the STM chamber [4].

Figure 1 shows STM images of a Si(001) surface covered with 0.11 ML C. The striking features for both filled states (sample bias −2 V, current 0.2 nA) and empty states (+2 V, 0.2 nA; see inset) are the elongated pairs of bright spots that are arranged into patches of a $c(4 \times 4)$ superstructure. In between these areas, the surface exhibits a Si buckled dimer reconstruction. Both reconstructions can coexist in the same atomic layer. An enhancement of surface roughness is observed for the C covered surface compared to the initial pure Si(001) (2×1) surface. The number of the paired spots changes drastically with the amount of deposited carbon. At 0.05 ML C only a few such pairs are found, mainly at step edges. The remaining Si surface consists entirely of buckled dimers instead of symmetric dimers on bare Si(001) (2×1). This is known to be caused by the presence of impurities [5], C atoms in our case. At 0.11 ML, however, already more than 10% of the surface is covered with the $c(4 \times 4)$ pattern. This demonstrates that the formation of the $c(4 \times 4)$ reconstruction is definitely caused by the C deposition [6]. Moreover, a certain number of C atoms has to come together within a

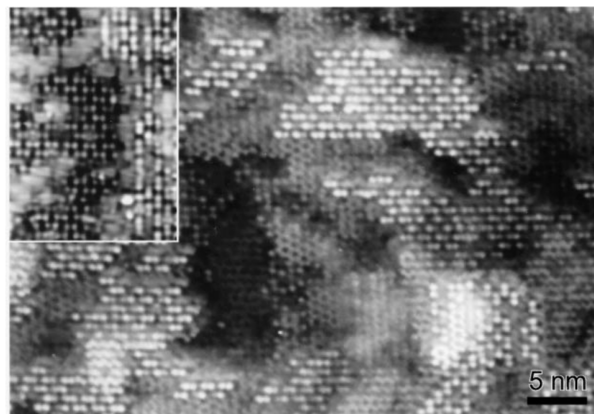

FIG. 1. Filled state STM image (−2 V, 0.2 nA) after deposition of 0.11 ML C on Si(001) at 550 °C. Areas covered with elongated bright spots lying in ⟨110⟩ directions exhibit a $c(4 \times 4)$ structure. The inset shows empty state data (+2 V, 0.2 nA), which exhibits essentially the same paired spot pattern.

 0031-9007/99/82(5)/972(4)$15.00 © 1999 The American Physical Society

$c(4 \times 4)$ unit cell to produce the superstructure, arranged either on surface or subsurface sites, which is much more likely to occur at higher coverage. Our findings are very similar to those reported recently by Butz and Lüth [11].

The curious feature in the STM images that is difficult to explain is the presence of two bright spots per $c(4 \times 4)$ surface unit cell, at an apparent height of about one ML. The two spots appear in pairs with an intrapair distance equal to 5.9 Å and an interpair distance of 9.6 Å. The distance between successive pair centers is 15.5 Å, which is the normal length of 4 times the basic repeat distance on the unreconstructed (001) surface ($4a_{0(\mathrm{Si})}/\sqrt{2}$; $a_{0(\mathrm{Si})} = 5.43$ Å). The intrapair distance is far too long to correspond to any kind of interatomic bond. Furthermore, the surface unit cell covers eight lattice sites. These observations argue that the bright spots cannot be associated with single atoms. We propose that the paired spot structure corresponds to two Si dimers, which would normally be at a second neighbor distance, i.e., 7.7 Å apart, and have come closer together at a distance of 5.9 Å due to strain induced by incorporation of substitutional C atoms in the Si lattice.

Still, the displacement of the Si dimers by 1.8 Å towards each other is a very significant distortion and cannot be easily rationalized. To account for this distortion we have considered a number of structural models that could potentially produce the desired effect. The presence of the dimer reconstruction on the Si surface produces a pattern of strain in the substrate, with certain sites (those directly under the surface dimers) under compressive stress, and other sites (those between dimer rows) under tensile stress. This pattern of opposite stresses can lead to interesting ordering effects in semiconductor alloys [12]. However, the very large strain induced by substitutional C atoms is such that a very strong repulsion results between C atoms at first neighbor sites below the top two surface layers. This repulsion can substantially reduce the ordering produced by the surface reconstruction [13]. We have taken all these considerations into account when constructing models that could potentially reproduce the experimental features. We illustrate the important features of the models we have considered in Fig. 2. We assume that there is at least one missing dimer from the surface layer, i.e., in the $c(4 \times 4)$ unit cell there are at most three surface dimers. The remaining dimers are made up from atoms at the top sites labeled A, B, and C in Fig. 2. Sites D and E lie in the second layer. The sites labeled F, G, H, and I in the third layer and site J in the fourth layer are all under compressive stress due to the surface reconstruction.

Eight different models were considered with different amounts of carbon atoms incorporated in the Si lattice (Table I). The models fall into two groups: in the first group [models (a)–(f)], the sites labeled B are unoccupied. The remaining two dimers at sites A and C are either silicon or carbon dimers. In the second group [models (g)–(h)], the sites labeled B are occupied by carbon atoms, i.e., there are three dimers in the unit cell, two Si dimers and one carbon dimer. The sites not being labeled are always occupied by Si atoms. The placement of C atoms in the different sites was guided by two considerations: (i) Carbon atoms were placed in sites that are compressively stressed due to the surface reconstruction, and (ii) they were situated in positions that are likely to lead to a pairing of the two Si dimers at sites A and C, which could then explain the observed STM images.

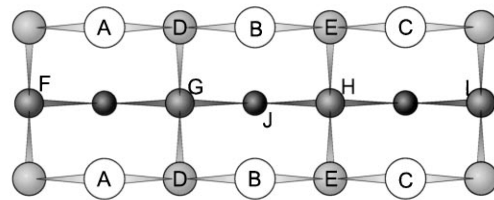

FIG. 2. Schematic top view of the atomic arrangement along the diagonal of a $c(4 \times 4)$ unit cell in the unreconstructed case. The atoms of the topmost four atomic layers are represented by circles, decreasing in size and brightness from top to bottom. The labeled atoms are those considered in the different models according to Table I.

In models (a)–(d), there are only two surface dimers which are composed of two Si atoms each, with various amounts of C atoms at sites F–J, placed so as to induce subsurface distortions that could potentially bring the surface Si dimers closer together. In model (e) both surface dimers are composed of C atoms. In model (f) one surface dimer is composed of C atoms and the other of Si atoms; the latter model also has two C atoms in the third layer. Model (g) has three surface dimers, the outer two of them composed of Si atoms at sites A and C, and the middle one composed of carbon atoms at site B. The shorter bond of this latter dimer will induce strain that could bring the Si dimers closer together. Finally, model (h) has the same atomic arrangement at the surface as model (g), and in addition has carbon atoms at the subsurface sites D and E. This introduces altogether five carbon-carbon bonds in a complex of six C atoms, which will induce a strain that will pull atoms around this complex closer to its center.

TABLE I. Occupation of surface and subsurface sites identified in Fig. 2 by silicon or carbon atoms. A dash (−) indicates the site is unoccupied.

Structure	Site									
	A	B	C	D	E	F	G	H	I	J
(a)	Si	−	Si	Si	Si	C	Si	Si	C	C
(b)	Si	−	Si	Si	Si	C	C	C	C	Si
(c)	Si	−	Si	Si	Si	C	C	C	C	C
(d)	Si	−	Si	Si	Si	Si	C	C	Si	C
(e)	C	−	C	Si	Si	Si	Si	Si	Si	Si
(f)	Si	−	C	Si	Si	C	C	Si	Si	Si
(g)	Si	C	Si	Si	Si	Si	Si	Si	Si	Si
(h)	Si	C	Si	C	C	Si	Si	Si	Si	Si

We have evaluated the models described above by investigating the energetics and the thermodynamic stability. We also evaluate the electronic charge densities on the surface, based on DFT calculations (the computational parameters are the same as in Refs. [13,14]). Gray-level plots of the surface charge density distributions of all models are depicted in Fig. 3. They were created using an energy window of 2.5 eV below the Fermi level, thus simulating STM images with about -2 V sample bias. We restrict our calculations to occupied states, as the experiment shows that the $c(4 \times 4)$ structure we consider here is only a little sensitive to the bias sign. In both cases the same overall image is obtained. The charge density contours have been convoluted with a Gaussian to account for limited STM-tip resolution in experiment. Some interesting features appear in these figures. In all cases the two surface dimers appear more or less asymmetric, which is a result of the asymmetric relaxation of the surface atoms. In cases (e)–(h), where there are one or two surface dimers composed of carbon atoms, these are not visible. Even in case (e), where there are just two C dimers on the surface, what is visible are their back bonds to their nearest neighbor Si atoms. This interesting effect, i.e., the invisibility of C-C dimers to STM when Si-Si dimers are also present on the surface, is due to the lower geometric position of the atoms and the lower energy of the bonding states of the C-C dimers (see also Ref. [14]).

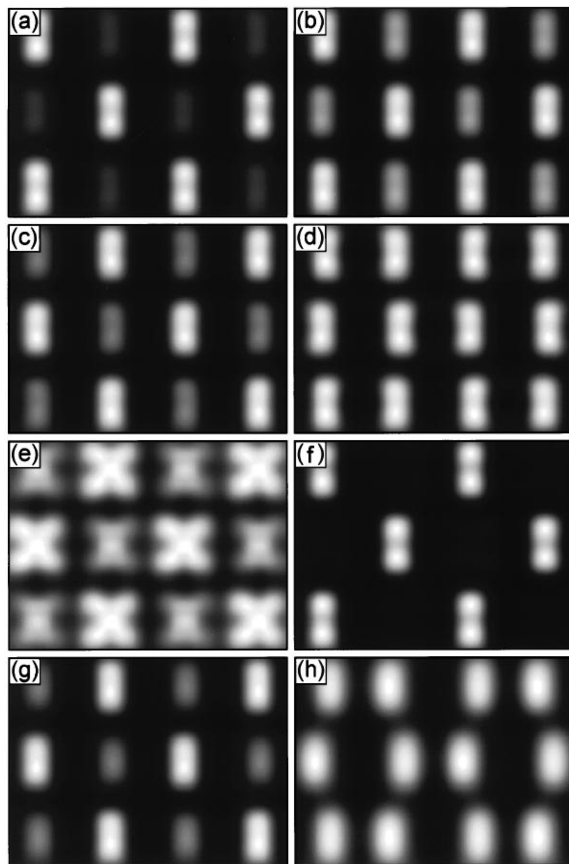

FIG. 3. Calculated surface charge density distributions of the models (a)–(h), corresponding to simulated STM images for occupied states. Bright white indicates high charge density. Only structure (h) is consistent with the observed STM images.

Of all the models examined, we find that only in model (h) are the surface Si dimers displaced sufficiently towards each other to form effectively a pair of dimers. In this structure, the surface Si dimers have been brought closer together by approximately 1.8 Å, in excellent agreement with the apparent distance of the bright spots in the experimental STM images. This displacement of the Si dimers is a consequence of the strain induced by the carbon atoms at sites B, D, and E. We therefore propose that the STM images could be interpreted as corresponding to this unusual structure, involving two Si dimers in the surface $c(4 \times 4)$ unit cell, brought considerably closer together due to the presence of a complex of six C atoms between the Si dimers, arranged in a surface carbon-carbon dimer and its first four subsurface neighbors.

Figure 4 displays a contour plot of the charge density in a vertical plane through the center of the rows of paired Si dimers for model (h). A scheme of the atomic arrangement in this plane comprising the topmost four atomic layers is also depicted, which demonstrates the displacement of the Si dimers and the C complex with respect to bulk positions. With increasing distance from the surface dimers (i.e., decreasing charge density) the corrugation of the contours decreases, and the only features that remain are the maxima directly above the two Si-surface dimers. The experimental line scans reproduce the calculated contours quite well, namely, the maxima positions coincide exactly, supporting the validity of model (h). As the actual distance of the STM tip above the surface is not known and the convolution of the tip with the contours is not included in the calculations, the corrugations of the line scans cannot be quantitatively compared. The decreasing corrugation with growing bias is due to increasing tip-sample distance.

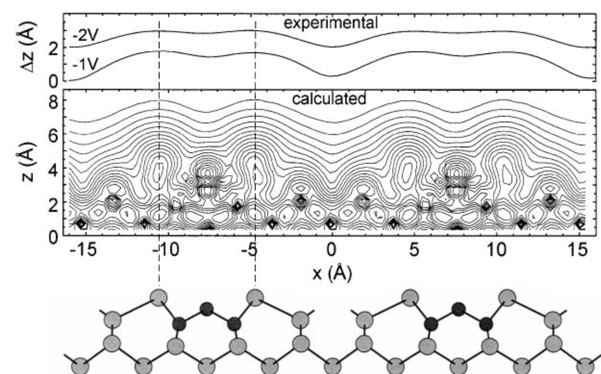

FIG. 4. Cross-sectional contour plot of calculated charge density in a vertical plane through the rows of dimer pairs for model (h). Values go from 0.191 $e^-/\text{Å}^3$ for Si-Si bonds to 2.7×10^{-6} $e^-/\text{Å}^3$ for the topmost line scan in the vacuum region. Experimental line scans are given above these for comparison. A schematic ball and stick model of the topmost four atomic layers is also shown. Si: light gray; C: dark gray.

A question to be taken into account is the entire amount of C atoms necessary for the observed $c(4 \times 4)$ area. This covers about 10%–12% of the surface for 0.11 ML C, as far as can be deduced from a limited number of atomic scale STM images assuming homogeneous deposition. If all C were contained in the $c(4 \times 4)$ regions, a number of eight C atoms would be available per $c(4 \times 4)$ unit cell. But it is very likely that a significant part of the deposited C atoms does not find enough neighbors to form a complex of six. These could then be incorporated in the areas between the $c(4 \times 4)$ regions, thus explaining the consistent buckling of the Si dimers. Therefore, a model having six C atoms per $c(4 \times 4)$ unit cell is compatible with experiment.

As another measure of the validity of our model, we have calculated and compared the total energies of the different structures. Since these contain different amounts of C atoms, it is important to compare their energies as a function of the chemical potential of carbon. This comparison is shown in Fig. 5. The carbon chemical potential ranges from 0 to 7.4 eV. These limits correspond to two extreme situations: In the first, the atomic reservoir for carbon atoms is a gas of free carbon atoms; in the second, the atomic reservoir is bulk diamond or graphite (the cohesive energy per atom of these two most stable forms of carbon is approximately the same, 7.4 eV [15]). For the energetic comparisons we take the atomic reservoir for Si atoms to be bulk Si, with which the surface is always in equilibrium, due to the presence of steps and other surface defects. For the systems we are considering, where carbon is deposited as monomers or larger clusters of carbon atoms (usually small, of size two or three), we believe the relevant range of carbon chemical potential is in the lower half of the entire range shown in Fig. 5. In this range, the lowest energy structure is by far model (h), which also gives the images that correspond most closely to the STM images. Finally, in an attempt to determine the thermodynamic stability of the proposed structure, we have done finite temperature simulations using the semigrand canonical Monte Carlo method with the use of empirical potentials to describe the atomic interactions [16]. We find that at a temperature of 600 °C, the structure is very stable against interchanges of C and Si atoms. At somewhat higher temperatures (we performed simulations also at 900 and 1200 °C), there is more of a tendency for interchange between the two types of atoms, although the rate of such atomic interchanges is rather small (approximately once in 10^5 Monte Carlo moves). Considering a temperature uncertainty in the simulations of -100 K and of -50 K for experiment, all these temperatures are equal or higher than typical growth temperatures of around 550 °C, leading us to suggest that if the structure we propose can be formed under usual growth conditions, then it will be stable.

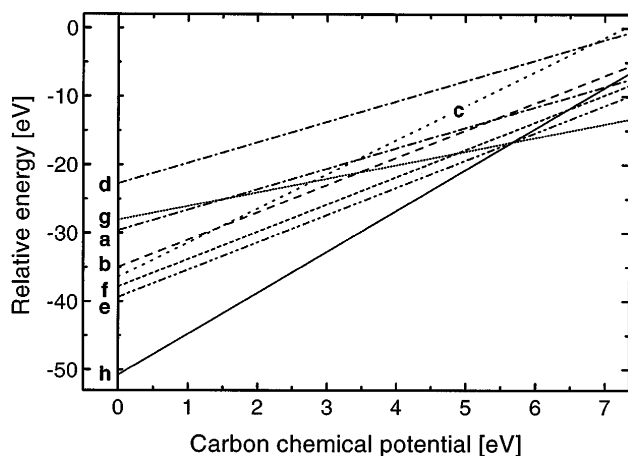

FIG. 5. Energy of the considered structures relative to a dimerized Si surface with one vacancy dimer per $c(4 \times 4)$ unit cell as a function of the carbon chemical potential. The lowest energy structure is by far model (h) in the range of chemical potentials relevant to experiment.

The work of E. K. is supported by an Office of Naval Research Contract No. N0014-95-1-0350. The calculations were performed at the Computer Center of the Physics Department, University of Crete, Heraclion.

*On leave of absence from the Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138.

[1] K. Brunner *et al.,* J. Cryst. Growth **175/176**, 451 (1997).
[2] O. G. Schmidt *et al.,* Appl. Phys. Lett. **71**, 2340 (1997).
[3] O. Leifeld *et al.* (to be published).
[4] O. Leifeld *et al.,* Appl. Phys. A **66**, S993 (1998).
[5] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).
[6] The observation of $c(4 \times 4)$ reconstruction on Si(001) has been reported by several authors after thermal treatment following an oxygen [7] or hydrogen [8] exposure or even pure thermal treatment [9]. It was usually assigned to a metastable pure Si structure. Only recently Miki *et al.* [10] suggested that it might have been caused by carbon impurities.
[7] F. K. Men and J. L. Erskine, Phys. Rev. B **50**, 11 200 (1994).
[8] R. I. G. Uhrberg *et al.,* Phys. Rev. B **46**, 10 251 (1992).
[9] H.-C. Wang, R.-F. Lin, and X. Wang, Phys. Rev. B **36**, 7712 (1987).
[10] K. Miki, K. Sakamoto, and T. Sakamoto, Appl. Phys. Lett. **71**, 3266 (1997).
[11] R. Butz and H. Lüth, Surf. Sci. **411**, 61 (1998).
[12] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989).
[13] P. C. Kelires and E. Kaxiras, Phys. Rev. Lett. **78**, 3479 (1997).
[14] P. C. Kelires and E. Kaxiras, J. Vac. Sci. Technol. B **16**, 1687 (1998).
[15] The theoretical cohesive energy is 50% larger, since typically LDA underestimates atomic energies. We believe it is more realistic to use the experimental cohesive energy.
[16] P. C. Kelires, Phys. Rev. Lett. **75**, 1114 (1995); Appl. Surf. Sci. **102**, 12 (1996).