Initial Stage of Carbon Incorporation into Si(001) and One-Dimensional Ordering of Embedded Carbon

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(Received 11 June 2002; published 20 August 2002)

We investigate the initial stage of the C incorporation into Si(001) using thermal dissociation of C_2H_2. The scanning tunneling microscopy shows that C-induced dimer vacancies (DVs) with depressed adjacent dimers are generated on the surface and aligned in the dimer direction, forming the $2 \times n$ structure. The *ab initio* pseudopotential calculations reveal that, with the presence of a DV in the surface, the α site in the fourth subsurface layer directly below the DV is the most favorable for the incorporated C atoms. The embedded C atoms align one dimensionally due to the interaction which is attractive in neighboring dimer rows but repulsive in the same dimer row.

DOI: 10.1103/PhysRevLett.89.106102 PACS numbers: 68.35.Dv, 68.35.Bs, 68.37.Ef

Carbon incorporation into Si(001) has attracted much attention due to the important role of carbon in developing high-performance, Si-based devices. The isovalent C atoms may induce systematic surface strains for building nanostructures on Si(001) without the doping effects. For instance, C atoms near the Si(001) surface can reduce the sizes of the Ge quantum dots [1,2] and play a major role in tailoring the band gap and mechanical properties of $Si_{1-x-y}Ge_xC_y$ [3–7]. They may be useful in altering the surface properties of Si(001) to prepare the suitable interface between Si and organic molecules [8,9]. However, the extremely low solubility of C atoms in bulk Si (below $10^{-3}\%$) has been considered as an obstacle to such applications. Recently, the $Si_{1-x}C_x$ films were synthesized at low temperature and high-growth rate with C concentrations over a few percent [10–13]. Theoretically, Tersoff showed that the presence of the surface and the surface reconstruction can significantly enhance the solubility of C atoms near the Si(001) surface [14].

The incorporated C atoms are generally agreed to be within a narrow region near the surface, but the exact location of C atoms is still under debate. Experimental studies are at variance, from surface [15] to subsurface [11] sites. *Ab initio* calculations are also varying in the preference between the surface and the subsurface incorporation. For a single C incorporation, either a surface Si-C heterodimer (HD) [16,17] or a third-layer α site [18] is calculated to be the lowest-energy configuration. Regarding two incorporated carbons, either one HD *plus* a fourth-layer carbon [17] or two surface HDs [18] were found to be most stable. However, it should be noted that all the previous calculations were performed under the assumption that the Si dimers are preserved upon C incorporation. The presence of C atoms in the Si(001) surface layers is likely to cause a significant surface stress. As a consequence, there is always a possibility of the surface modification to relieve the stress and the concurrent change of the most stable C-incorporation sites.

In this Letter, we demonstrate that the surface modification does occur upon C incorporation into Si(001). By combining the scanning tunneling microscopy (STM) and the *ab initio* calculations, we found that, in the initial stage of the C incorporation, all the C atoms occupy the α site in the fourth subsurface layer and induce Si dimer vacancies (DVs) directly above them. The composites of a fourth-layer C and a Si DV arrange themselves into quasi-one-dimensional rows in the dimer direction, forming the $2 \times n$ structure at C concentration of about 0.05 monolayer (ML).

Experiments were performed using a STM in an ultrahigh vacuum chamber with the base pressure below 1.2×10^{-10} Torr. The clean Si(001) surface was prepared with the conventional recipe [19]. We used C_2H_2 gas as the C source [20], taking advantage of high sticking probability and efficient thermal dissociation. The C_2H_2 gas was dosed on the Si(001) surface at room temperature by backfilling the vacuum chamber at 1×10^{-9} Torr with various dosing times. The adsorbed C_2H_2 was dissociated by heating the surface at temperatures between 700 and 1000 K for 2 min. All the STM measurements were made at room temperature. Before heating, we counted the number of the adsorbed C_2H_2 molecules based on the identified STM features [20]. The C concentration was estimated by repeated comparisons between the flux of C_2H_2 gas and the number of adsorbed C_2H_2 molecules, assuming the thermal dissociation probability of 95% [21].

Figures 1(a) and 1(b) show the STM images of the C-incorporated Si(001) surface with C concentrations of about 0.02 and 0.05 ML, respectively, [$1\ \mathrm{ML} = 6.8 \times 10^{14}\ \mathrm{atoms/cm^2}$, corresponding to the density of topmost Si atoms in the clean Si(001) surface]. In the images, DV-like features are commonly observed and their density increases with the C concentration. They are aligned in the dimer direction to form short chains [Fig. 1(a)] which grow in length and finally construct $2 \times n$ structures at around 0.05 ML [Fig. 1(b)] [22]. The

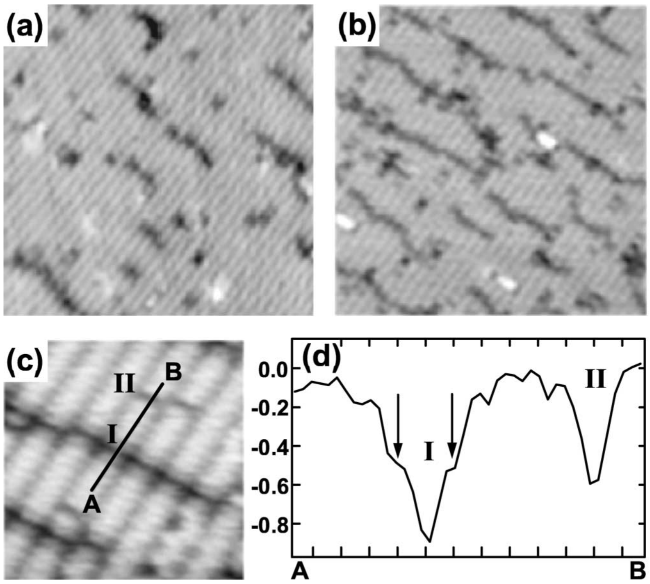

FIG. 1. Filled-state STM images of a Si(001) surface with (a) 0.02 and (b) 0.05 ML of C concentration. (c) The magnified STM image of a DV line comprising the 2 × n structure. (d) The height profile (Å) along $\overline{AB}$ in (c). Note that there exists depression of two dimers (indicated by ↓) adjacent to the C-induced DV (I), differing from the normal Si DV (II).

density of the DV-like features is proportional to the C concentration with a ratio close to *unity.*

The observed DV-like features are not the same as the normal Si DV frequently found on the clean Si(001) surface. As seen in the magnified image of Fig. 1(c), each DV-like feature is composed of one DV and *two symmetrically depressed neighboring dimers* on both sides along the dimer row. The height profile in Fig. 1(d) reveals that the magnitude of the depression at the two neighboring dimers is about 0.5 Å. Notice that the normal Si DV [II in Figs. 1(c) and 1(d)] present in the same dimer row does not show these depressions.

There has been no report on such a DV accompanied by two neighboring depressed dimers, to the best of our knowledge. For instance, the DV features in the compressively strained Ge/Si(001) surface [23] or in the Ni-contaminated Si(001) [24] are quite different from those observed in this work, though they form similar 2 × n structures. The 2 × n structure on the Ge/Si(001) surface consists of single-DV channels without depression of the neighboring dimers. On the other hand, the defect channels on the Ni-contaminated Si(001)-(2 × n) surface are mainly composed of the normal DV clusters such as 2 or (1 + 2) DVs. Therefore, the unique appearance of the features in Fig. 1(c) strongly suggests that they are caused by the C incorporation.

Our observations can be summarized into three: (i) the one-to-one proportionality between the DV-like features and the incorporated C atoms, (ii) the DV *plus* symmetric depression at two neighboring dimers, and (iii) the magnitude of depression (0.5 Å) close to the bond-length difference between Si-Si and Si-C. These observations impose constraints that should be satisfied by the structural models for the C incorporation. The most plausible C site that meets the above conditions is the substitutional α site in the fourth subsurface layer, directly under the DV. A single C atom at any other subsurface site is not compatible with the observed symmetric appearance.

To confirm our conjecture on the C-incorporated Si(001) surface, we performed the *ab initio* pseudopotential calculations within the local-density approximation (LDA), using the Vienna *ab initio* simulation package [25]. We used a plane-wave cutoff of 300 eV, the theoretical lattice constant of 5.39 Å, and ultrasoft pseudopotentials [26]. The dimerized Si(001)-$p(2 \times 2)$ surface was modeled by a ten layer slab separated by 8 Å vacuum. The bottom surface was passivated by hydrogens. The Si atoms in the bottom two layers and the H atoms were fixed, while the rest of the atoms were allowed to relax until their rms forces were smaller than 0.02 eV/Å.

First, we consider the case of the single C atom incorporation. For that purpose, we used a $c(8 \times 8)$ surface supercell to reduce the intercell interaction. The Brillouin zone integration was performed using Γ-point sampling. For various C-substitution configurations both with and without a Si DV [see Fig. 2(a)], the calculated total energies are plotted in Fig. 2(b). The results for the configurations preserving the surface Si dimers are in agreement

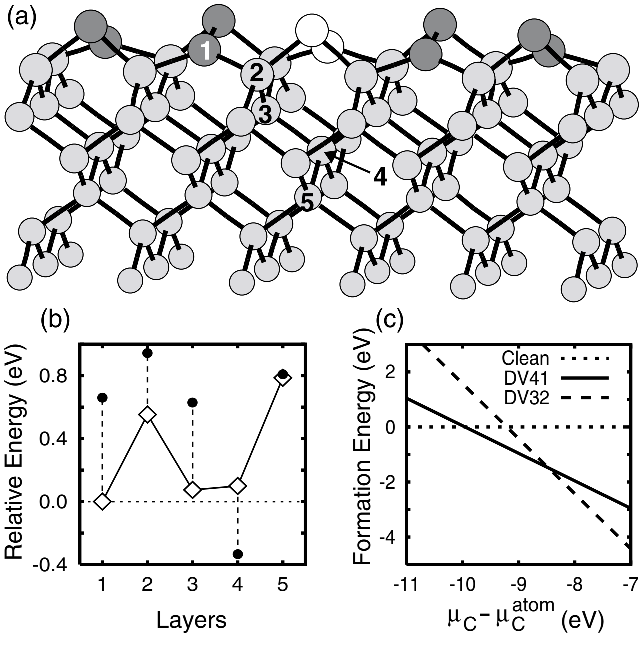

FIG. 2. (a) Atomic structure of Si(001) with the C substitution sites indicated by the corresponding layer indices. The Si dimers are represented by dark grey circles. The white circles are the Si atoms to be removed in creating a DV. (b) The relative energies of different single-carbon incorporation configurations. ◇ and • are for the intact dimer and the missing dimer configurations, respectively. (c) The formation energies for the configurations of single- and two-carbon incorporation with Si DV.

with the previous calculations by Sonnet *et al.* [17], but differ from the results in Refs. [16,18]. The surface substitutional site is found to be preferentially occupied by C atoms to form a Si-C HD. The third- and the fourth-layer sites are slightly higher in energy, but the second- and the fifth-layer sites have much higher energy. This trend, however, changes dramatically as soon as we take into account the possibility of a Si DV creation. With a DV, total energies for the substitutional sites [labeled by 1, 2, 3, and 5 in Fig. 2(a)] at the first, the second, the third, and the fifth layer are increased by 0.66, 0.39, 0.56, and 0.02 eV, respectively. In contrast, *the C substitution at the fourth layer is stabilized by 0.43 eV in creating a DV directly above the C atom and becomes the lowest-energy configuration*. We will name this configuration as DV41 throughout the paper. The adjacent two Si dimers relax downward by 0.4 Å, which is in accordance with the characteristics of the STM height profile shown in Fig. 1(d). The origin of the exceptional energy lowering in the case of DV41 will be discussed later.

To verify that there is no more than a single-carbon associated with the DV-like STM feature, we then investigated two-carbon incorporation. Considering the symmetric appearance of the STM feature, there are only two configurations possible: two-carbon atoms at the third layer (DV32) and at the fifth layer (DV52). DV52 is found to be higher in energy by 1.1 eV than DV32. Now we compare the formation energies as a function of the C chemical potential as plotted in Fig. 2(c). In the very initial stage of C incorporation, DV32 is not stable at all with respect to DV41. This assures that DV32 is not the structure for the observed STM feature. As a matter of fact, DV32 is less stable by 0.8 eV than the two-neighboring-HD configuration which was calculated to be the lowest-energy two-carbon configuration in Ref. [18]. This instability of DV32 (and DV52) is related with the fact that two-carbon atoms occupy second nearest-neighbor sites. It is worthwhile to note that any configuration with two C atoms closer than the third nearest neighbor has been considered to be energetically unfavorable [11,18]. We also checked another two-carbon configuration which was claimed to be the lowest-energy configuration by Sonnet *et al.* [17]. It is composed of a single Si-C HD and a fourth-layer carbon below a Si dimer adjacent to the HD. This configuration is less stable than the two-adjacent-HD configuration by 0.08 eV, opposing the results in Ref. [17]. We attribute this discrepancy to the usage of the $c(4 \times 4)$ cell in Ref. [17] compared to the 4 times larger $c(8 \times 8)$ cell used in this work. In other words, the $c(4 \times 4)$ supercell is too small to accommodate the strain induced by two incorporated carbon atoms.

Now we examine the aligning tendency of incorporated C atoms. For that, we prepared a $p(4 \times 8)$ supercell with two dimer rows as shown in Fig. 3(a) and created a DV41. Then we created the second DV41 at locations either on the same dimer row [Am in Fig. 3(a)] or on the adjacent row [Bm in Fig. 3(a)], where m stands for the projected distance (ma, where a is the surface lattice constant) along the dimer row direction between the first and the second DV41s. The relative total energies in Fig. 3(b) show that, in the same dimer row, two DV41s interact strongly repulsively. On the other hand, DV41s attract each other when they are placed in two neighboring dimer rows. These results imply that incorporated C atoms prefer to align with each other along the dimer direction and form DV lines, where the embedded C atoms occupy every fourth nearest-neighbor sites (with the intercarbon distance of 7.68 Å). Owing to the repulsive interaction in the same dimer row, these DV lines cannot come closer than a certain distance na to each other and result in the $2 \times n$ structure as observed in Fig. 1.

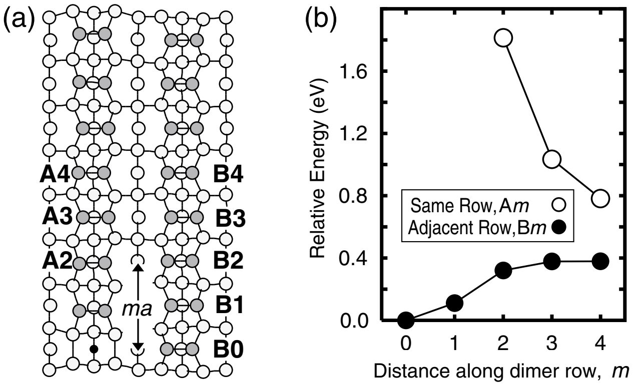

FIG. 3. (a) The schematic diagram of $p(4 \times 8)$ supercell with one DV and a fourth-layer C atom (solid circle). The sites for the second DV41 are labeled by Am in the same dimer row and Bm in the adjacent dimer row. (b) The relative energies of two DV41s as a function of m.

As a final step to examine our model, we have simulated the constant-current STM images within Tersoff-Hamann approximation [27] using the relaxed atomic coordinates of the configuration B0 in Fig. 3(a). In order to simulate the symmetric dimers at room temperature, the LDA images from the oppositely buckled dimers were averaged. Both the LDA and the experimental images shown in Fig. 4 for the negative and the positive biases are in good agreement, showing the depression at dimers adjacent to DV41.

The change of the most stable C-incorporation site, from the surface for the intact surface to the fourth-layer α site for the surface with a DV, can be understood intuitively.

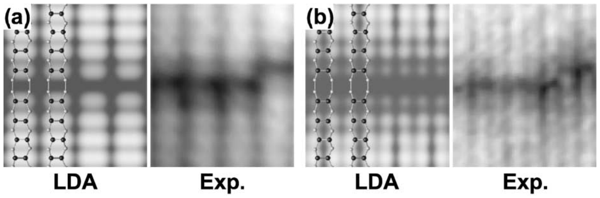

FIG. 4. Typical STM images of (a) filled state ($V_s = -2.5$ V) and (b) empty state ($V_s = +1.5$ V). The simulation clearly reproduces the observed depression at dimers adjacent to C-induced DV. The kinks in the experimental images help to locate dimer rows.

When C is incorporated, a large stress is built up for the nearby Si atoms due to the difference in atomic size between C and Si. In the case of the Si(001) surface with dimers intact, the C-induced stress can be partially relieved via two ways. One is the relaxation of the neighboring Si atoms, which can be more effective on the surface. The other is C substitution at α sites under the compressive stress caused by the surface dimerization, and this is the case for the third and the fourth layers. The results of our calculations show that the former can reduce the total energy more effectively, as evidenced by the fact that the surface Si-C HD is the lowest-energy configuration.

The total energy can be further lowered by creating a DV in the case of C incorporation at the fourth-layer α site. In this case, the fourth-layer C imposes the compressive stress on the Si dimer above it. Thus, the stress induces a dimer vacancy and enforces subsequent rebonding of the second-layer Si atoms (the bond-length of the rebonds, 2.54 Å, is shorter than 2.63 Å in the normal Si DV). This energy gain from the enforced rebonding overwhelms the energy cost from the removal of a dimer, making the configuration with DV more stable than one without DV. In consequence, the DV41 becomes lowest-energy configuration for a single C incorporation. The other substitutional C sites are not benefited by the creation of DV. For instance, for the first- and the second-layer sites, only one rebond is formed in the second layer leaving two dangling bonds and, thus, the total energy is increased. For the third- and fifth-layer C sites, the two weak rebonds are formed but the resulting energy gain does not compensate the energy cost of the dimer removal.

By combining the STM and the *ab initio* calculations, we conclude that, at the initial stage of incorporation into the Si(001) surface, C atoms prefer to occupy the fourth-layer α site and create a Si DV directly above them. This conclusion contrasts to those of the previous theoretical studies based on a hypothetical surface without DVs. The incorporated C atoms interact attractively on neighboring dimer rows, but repulsively on the same dimer row. In consequence, a $2 \times n$ structure with DV lines is formed. In this C-incorporated Si(001)-$2 \times n$ structure, a tensile-strained δ-like $\mathrm{Si}_{1-x}\mathrm{C}_x$ structure is realized in the fourth subsurface layer.

This work was supported by the Ministry of Science and Technology of Korea through the Creative Research Initiative, and in part by the Korea Science and Engineering Foundation through the ASSRC at Yonsei University. The calculations were performed through the Grand Challenge program of the KISTI.

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