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# Carbon induced restructuring of the Si(111) surface

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We present a combined experimental and theoretical investigation of the early carbonization stages of the Si(111)-(7×7) surface upon acetylene exposure. Scanning tunneling microscopy images reveal the formation of a $(\sqrt{3}\times\sqrt{3})$R30° reconstruction. *Ab initio* calculations allow us to characterize this reconstruction as a carbon-rich silicon phase due to subsurface incorporation of C atoms.

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The study of the interaction between small molecules containing carbon (such as acetylene) and Si surfaces has deserved a large amount of work in recent years, both from the theoretical and experimental points of view. An interesting point is the experimental evidence of the formation of SiC films on Si substrates obtained by exposure to these C-containing molecules, without further supply of silicon.[1–6] The mechanism governing the growth process is still a subject of debate, although recently[7,8] the adsorption geometries of acetylene molecules at the Si(111)-(7×7) surface have been investigated, and a possible mechanism for the dissociation of acetylene through interaction with silicon atoms from the substrate has been suggested.[8] Moreover, there is a wide interest on the realization of carbon-enriched silicon structures for optoelectronic applications: the success in growing these systems is hindered by the low solubility of carbon in silicon at thermodynamic equilibrium. Preliminary experimental results[9] have shown that an unexpectedly high concentration of carbon can be achieved in surface or subsurface Si(111) layers, via deposition at relatively low ($\simeq 600\,^\circ$C) temperatures. While theoretical and experimental results confirm the possibility of enhancing the carbon incorporation at Si(001) surfaces,[10] a detailed theoretical investigation of the effects of carbon atoms adsorbed on the Si(111) surface is still lacking. An empirical calculation[11] suggested that possible adsorption sites for atomic carbon may occur at the Si surface (in the H3 hollow site, see Fig. 1) or at the subsurface substitutional S5 site, while carbon clusters should preferably appear around S5. Thus the subject on site stability and carbon concentration is still controversial.

Here we focus on the early carbonization stages of the Si(111)-(7×7) surface induced by exposure to a flux of acetylene at $\simeq 600\,^\circ$C. We performed a combined experimental and theoretical investigation to clarify the preliminary results reported in Ref. 12, and to study more relevant incorporation rates. Our findings indicate that the adsorption of acetylene molecules at the Si(111) surface results in the removal of the 7×7 reconstruction in favor of a novel $\sqrt{3}\times\sqrt{3}$ one, similar to that observed for boron inclusions in Si(111).[13–17]

Real time scanning tunneling microscopy (STM) images of a Si(111)-(7×7) reconstructed surface were acquired during acetylene exposure at $600\,^\circ$C. The surface was prepared from phosphorous-doped Si(111) wafers (nominal resistivity $\simeq 0.3$–$0.5\ \Omega$ cm), which were intentionally studied, to avoid any spurious effect induced by boron doping.[13–17] The samples were heated *in situ* by Joule effect at 1200 °C; after this annealing, no traces of reconstructions different from the 7×7 were observed even close to step edges. The wafers were kept in ultrahigh vacuum ($2\times10^{-8}$ Pa) during heating, and STM images were obtained after 60, 120, 180, and 360 L of acetylene exposure. A detailed description of the experimental method is given in Ref. 12.

The STM images that we recorded reveal the progressive removal of the 7×7 reconstruction at the surface. Already after 60 L exposure (Fig. 2), the step edges begin to appear irregular with atomic protrusions changing their original straight and abrupt shape. This gives rise to a progressive corrosion of terrace areas and leads to the formation of large inlets, with increasing acetylene doses. This reaction process, leading to a substitution of the original 7×7 reconstruction with a $(\sqrt{3}\times\sqrt{3})$R30° surface arrangement, starts in regions close to step edges; then it progressively expands throughout the upper terraces[12] with increasing carbon amount. A similar expansion mechanism eventually involves also the surface regions where preexposure defects or holes exist.

Low-energy electron diffraction (LEED) patterns recorded after 360 L exposure show a coexistence of (1×1) and $(\sqrt{3}\times\sqrt{3})$R30° spots [see Fig. 2(c)]. By comparing the

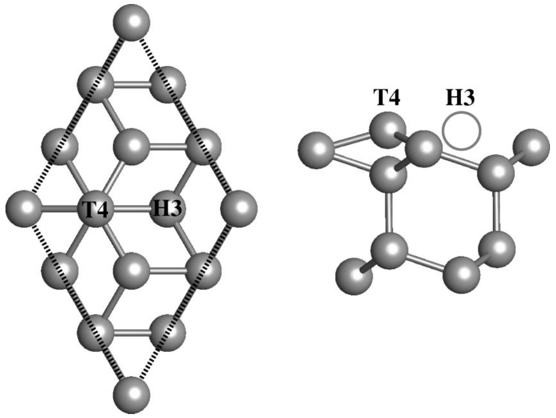

FIG. 1. Schematic top (left) and side (right) view of the $\sqrt{3}\times\sqrt{3}$ reconstruction.

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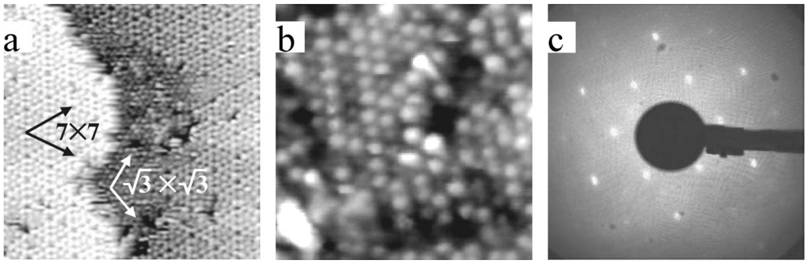

FIG. 2. STM (a,b) analysis of the Si(111) surface after acetylene exposure (filled states, $V_{bias}=-2.0$ V, $I_{tunnel}=1.8$ nA). In (a) ($30\times30$ nm$^2$), a portion of the original clean 7×7 reconstruction is still clearly recognizable together with the $\sqrt{3}\times\sqrt{3}$ zone. Arrows parallel to the basis vectors for the 7×7 and $\sqrt{3}\times\sqrt{3}$ reconstructions are drawn in the corresponding regions. A magnified snapshot ($10\times10$ nm$^2$) of a zone with a $\sqrt{3}\times\sqrt{3}$ reconstruction is shown in (b). (c) is the LEED pattern after completion of C incorporation (360 L exposure), with the $\sqrt{3}\times\sqrt{3}$ reconstruction already stabilized.

reciprocal lattice spots, we evaluated that the lattice parameter of the latter surface reconstruction is about 0.65 ±0.08 nm. This result is confirmed by measuring the interatomic distances along the main directions of the ($\sqrt{3}\times\sqrt{3}$)R30° surface cell in the STM images (0.66 ±0.02 nm). Since the silicon terminated hexagonal SiC(0001) ($\sqrt{3}\times\sqrt{3}$)R30° surface reconstruction is characterized by an adatom distance of 0.53 nm,[18] our reacted compound cannot be silicon carbide but rather a different Si(111) phase induced by carbon incorporation, in agreement with previous results obtained by means of atomic carbon deposition.[9]

A result analogous to our findings was already reported in the literature for the incorporation of boron in Si: LEED (Ref. 13) and STM (Refs. 14–16) studies evidenced that adsorption of boron atoms on the Si(111)-(7×7) surface may result in the removal of the reconstruction, towards the formation of domains of adatom-covered regions with $\sqrt{3}\times\sqrt{3}$ periodicity. At variance with other group III elements on Si(111),[19] the superstructure induced by boron incorporation appears as dark spots in STM empty states images, thus suggesting that boron occupies subsurface sites. This evidence was supported by calculations indicating that the preferred site for B at the surface is the S5 substitutional site below the Si adatom in T4.[14]

To shed light on the nature of the carbon enriched Si reconstruction observed experimentally, we performed *ab initio* density-functional calculations to investigate the energetics of different configurations for C incorporation in the Si(111) surface. We considered both a 2×2 and a $\sqrt{3}\times\sqrt{3}$ reconstruction: the choice of performing calculations on a 2×2 cell is suggested to describe in an accurate way the adatom–rest-atom couple of the 7×7 reconstructed surface, while reproducing the portion of surface where the original 7×7 reconstruction is removed.[8,20] This allows us to understand the mechanisms of C adsorption and Si substitution at low C coverages, before building up a complete $\sqrt{3}\times\sqrt{3}$ reconstruction. The electronic wave functions were expanded in plane waves, with energy cutoff of 50 Ry (for the 2×2 calculations). Electron-ion interaction was included via pseudopotentials; the Perdew-Wang[21] parametrization for the gradient-corrected exchange-correlation (GGA) functional was adopted. We modeled the surfaces through a repeated slab representation. For the 2×2 surfaces the slab is composed of six Si double layers with 4×4 periodicity and a hydrogen layer to saturate the dangling bonds of one of the slab surfaces; only the $\Gamma$ point was used for the Brillouin-zone (BZ) sums. In order to enhance comparison with the experimental STM images at high coverages, we performed further calculations in a $\sqrt{3}\times\sqrt{3}$ cell. This surface is characterized by three Si atoms per unit cell and an adatom in the tetrahedral T4 position, as indicated in Fig. 1. A similar technique has been adopted in this set of calculations, although in this case we used ultrasoft pseudopotentials[22] with 25 Ry cutoff energy, a slab with $\sqrt{3}\times\sqrt{3}$ periodicity, and a Monkhorst-Pack grid of 2×2 **k** points for the BZ sums. The relative stability of different structures was evaluated in the grand-canonical scheme.[23]

To interpret the experimental results, we considered first of all the adsorption of C atoms at the 2×2 surface. In order to understand if the preferred adsorption site lies above or below the surface, we calculated the energetics for different cases: adsorption of four carbon atoms in a T4 site (C-T4, substituting the Si T4 adatoms), and adsorption of four carbon atoms in an S5 site (substituting the four Si atoms below the four Si-T4: this structure will be hereafter labeled as C-S5). Our calculations evidenced that S5 is the preferred site for carbon incorporation: this structure is favored by 1.7 eV (per C atom, i.e., per 2×2 cell) with respect to the C-T4 structure. This result is in agreement with similar findings for boron atoms[14] and the empirical calculation for C:Si(111).[11] A further test calculation for a structure with a C atom in S5 and a C atom in T4 (per 2×2 cell) was found to lay 1 eV per C atom above C-S5. The energy differences are large compared to the error that can arise from the different **k**-point sampling[24] between this last one and the two other geometries.

In order to improve the comparison with experiment at larger incorporation rates, and provide a detailed description of the electronic and structural properties of the ($\sqrt{3}\times\sqrt{3}$)R30° reconstruction observed via STM, we performed further calculations in a $\sqrt{3}\times\sqrt{3}$ unit cell. Also in this case, the natural choices for C are T4 and S5. The simulations confirmed that the substitutional S5 site is the preferred one for C incorporation. For the sake of completeness, we furthermore considered other adsorption sites, substituting dif-

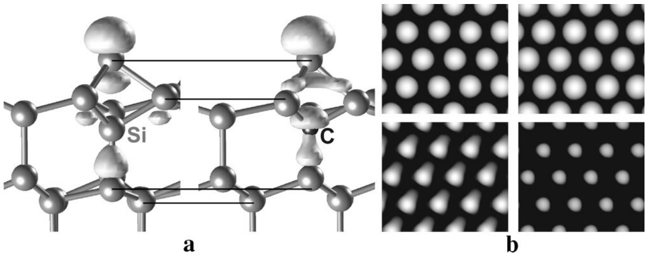

FIG. 3. (a) Side view of the Si(111) $\sqrt{3}\times\sqrt{3}$ slab. Only the Si bilayers that undergo significative displacements are shown. The reference lines evidence the different relaxation of the surface atoms for the geometries considered. From left to right the slabs correspond to the clean Si surface, with Si adatoms in T4, and to the C-S5 structure (one substitutional C atom in S5). The panels reproduce similar isosurfaces for the HOMO states at $\Gamma$. Gray (black) spheres are Si (C) atoms. (b) STM constant current simulated images for filled (top panels) and empty (lowest panels) states at $V_{bias}=-1.5$ V and 0.5 V, respectively, for the clean (right) and C-S5 (left) $\sqrt{3}\times\sqrt{3}$ reconstructed surfaces; the surface unit cell is replicated in each snapshot to facilitate comparison with experiments.

ferent surface Si atoms, or with the carbon adatom in H3. Also these geometries are metastable structures: substituting a surface Si atom leads to a configuration which lays 0.65 eV and 1.13 eV per C atom below configuration C-T4 and above configuration C-S5, respectively.[25] The structure with a carbon adatom in H3, instead, is not stable, and spontaneously evolves to recover a higher coordination for the carbon adatom, towards a distorted T4 geometry. This result, which contradicts the outcomes of empirical potential simulations,[11] should not be surprising, as it is known that classical potentials tend to stabilize a larger number of metastable structures compared to first-principles methods.[26] As discussed before, we evaluated the relative stability of the C-S5 configuration with respect to the clean $\sqrt{3}\times\sqrt{3}$ surface, in the grand-canonical scheme.[23] we found that carbon incorporation is always unfavorable, but for extremely C-rich and Si-poor conditions, where the C-S5 structure becomes almost degenerate (+0.04 eV/cell) with the clean surface reconstruction. This result is in agreement with the experimental evidence of poor solubility of C in Si bulk. In view of this result, we did not consider higher coverages for carbon: the present one (1/3 ML) already accounts for the observed $\sqrt{3}\times\sqrt{3}$ reconstruction.

In Fig. 3(a) we report the equilibrium geometries for the clean $\sqrt{3}\times\sqrt{3}$ surface with a Si adatom, and for the most stable structure containing carbon, i.e., C-S5. At a first inspection, it appears evident that there is not a large difference in the $z$ position of the Si adatoms in the clean surface and for the surface with C in S5; the Si surface atoms bonded to the adatom however move deeper in the bulk (0.26 Å, the Si-Si bond length varies from 2.45 to 2.51 Å) when C is adsorbed in S5. This relaxation occurs to optimize the C-Si distances, and it is in agreement with the charge transfer towards the carbon atom, as evidenced for instance by the highest occupied molecular orbital (HOMO) states, which are visualized in Fig. 3(a), for the clean and C-S5 surfaces. Both HOMO and lowest unoccupied molecular orbital, not shown, are localized on the Si adatom in both structures; however, for the defected C-S5 $\sqrt{3}\times\sqrt{3}$ surface, the states present larger components towards the subsurface S5 site (C atom) and at the Si adatom backbonds. This result implies that STM images should appear as broad, less contrasted spots in correspondence to substitutional C-S5 sites. This is evidenced in the top panels of Fig. 3(b), where the STM simulated images for filled states for the two structures are presented, in comparison with the calculated empty states images shown in the bottom panels: the applied voltage and current level are kept the same in the clean and C-S5 simulated images, to enhance relevant details. The empty and filled states images result complementary, as the C-S5 structure has darker STM spots in empty states, than the clean one. Zones with different brightness in the experimental images at constant current may thus be interpreted as portions of the sample where carbon substitution in subsurface sites has/has not occurred, rather than zones of different heights.

Our theoretical results compare well with the experimental STM images for filled states, reported in Fig. 2, and provide a detailed interpretation of the observed reconstruction. They are furthermore in agreement with the results obtained for boron:[14,17] although a group IV element carbon presents a high electronegativity value, much larger than that of silicon, with which it tends to make polar bonds, attracting the charge along the bond direction.[27]

In conclusion, we have found that adsorption of acetylene at the Si(111)-($7\times7$) surface may result in the removal of the $7\times7$ reconstruction in favor of a ($\sqrt{3}\times\sqrt{3}$)R30° reconstruction, in a similar way as observed for different precursors. The distances between corresponding maxima in the STM images reveal that the reconstruction does not correspond to the formation of a SiC film but to a Si reconstruction. Our *ab initio* calculation allows us to interpret the experimental findings in terms of a C-rich silicon phase: the carbon atoms arising from the dissociation of the adsorbed molecules occupy subsurface substitutional sites below the Si adatoms. The analysis of the electronic states has allowed us to characterize the different brightness of spots in the STM images. The mechanism of carbon incorporation that we have described may be an efficient way to perform an ordered carbonization of the silicon substrate, leaving a Si-terminated surface, which represents a favorable condition for subsequent SiC growth.

*Note added in proof:* Our results nicely compare to Xiangyang Peng, Ling Ye, Xun Wang, Surf. Sci. **548**, 51 (2004).

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[20] The $2\times2$ surface has four Si surface atoms and one adatom: the Si adatom is bonded to three of the surface atoms in a tetrahedral configuration (T4) on top of a subsurface Si atom; the Si surface atom not bonded to the adatom is called rest atom. The electronic and structural properties of the $2\times2$ cell well reproduce the adatom and rest-atom sites of the $7\times7$ reconstruction (Ref. 8): the rest-atom dangling bond is filled (partially filled in the $7\times7$) and the adatom–rest-atom distance is 4.57 Å (4.55 Å in the $7\times7$).

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[24] As induced by a different C concentration.

[25] The agreement in energy difference between configurations C-T4 and C-S5 from one set of calculations to the other is only apparent, as the normalization made on the number of substitutional carbon atoms per cell hydes a different cell size; furthermore, the **k**-point sampling and pseudopotentials are different. However, a consistency check allowed us to quantify a deviation in energy differences of $\simeq\pm0.06$ eV (per C atom) between the two different methods, which thus does not affect our conclusions.

[26] See, for instance, G. Cicero, L. Pizzagalli, and A. Catellani, Phys. Rev. Lett. **89**, 156101 (2002); C. Sbraccia, P.L. Silvestrelli, and F. Ancilotto, Surf. Sci. **516**, 147 (2002).

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