$\sqrt{3} \times \sqrt{3}\ R30° \rightarrow 3 \times 3$ distortion on the C/Si(111) surface

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Ab initio calculations performed on carbon-induced $\sqrt{3} \times \sqrt{3}R30°$ on the Si(111) surface reveal that C exchanges place with Si atoms belonging to the subsurface layer. As a result, the surface reconstruction is characterized by Si adatoms in the T_4 adsorption site. In analogy with the more general class of group IV adatoms on Si and Ge(111) surface, where the adatom is seen to induce a typical $\sqrt{3}$ reconstruction, we investigate the possible occurrence of a stable 3×3 reconstruction and find that the system is unstable upon adatom distortions. The C-induced 3×3 reconstruction on the Si(111) surface adds another interesting tile to the puzzle of surface phase transitions of group IV adatoms on Si and Ge(111) surfaces.

In the last few years, the physics of group IV adatoms on Si and Ge(111) surfaces has attracted great attention due to structural phase transitions observed at low temperatures. In fact, it is well known that 1/3 monolayer coverage of Sn or Pb on Ge(111) induces a $\sqrt{3} \times \sqrt{3}R30°(\sqrt{3})$ surface reconstruction, which goes into a 3×3 reconstruction at low temperatures.[1,2] The same $\sqrt{3}$ phase is observed at room temperature in similar systems as well, such as in Sn and Pb on Si(111). However, in these latter systems the low temperature phase was never observed [in the case of Sn/Si(111)] or is very debated (Pb/Si(111)).[3–5] A full understanding of the physical nature of this phase transition is still an open question, even though many theoretical models have been proposed so far. The occurrence of a charge density wave (CDW) phase,[1] stated at first as a possible driving mechanism, was quite soon ruled out due to the poor Fermi surface nesting found in all the systems considered. Among the others, some of the most recent and relevant theoretical models proposed invoked: (i) dynamical fluctuations,[6] that could be able to explain many controversial experimental evidences; (ii) correlation effects due to the relevant on-site Coulomb repulsion, within a Hubbard picture;[7] (iii) adatom-adatom interaction[8] mediated by electrons; (iv) mixed valence picture;[9] (iv) and a surface soft phonon mode[10] that might drive an order-disorder phase transition.

Recent first-principles calculations were able to establish that the 3×3 phase is the most stable phase at 0 K for both Pb/Ge(111) and Sn/Ge(111),[1,6,11] whereas in the Sn/Si(111) case, the ground-state phase is found to be the $\sqrt{3}$;[12,13] finally, in Pb/Si(111), the 3×3 seems to be a metastable[14] phase. All these different systems share the same physics: the group IV adatom saturates the three dangling bonds of the clean group IV (111) substrate surface, so that one half-filled dangling bond is left per $\sqrt{3}$ unit cell. As a result, the surface is metallic and shows a high density of states at the Fermi level. Thus, all the systems mentioned are supposedly good candidates for either a structural or an electronic phase transition. The physical evidence showing that the different systems do not exhibit the same phase at low temperature are, therefore, rather puzzling.

In this paper, we perform first-principles calculations to investigate the possible occurrence of the $\sqrt{3} \rightarrow 3 \times 3$ distortion on a candidate system; namely, carbon on Si(111) surface. Although carbon, as well as Si, Ge, Sn, and Pb, belongs to group IV, it is the only member of the family that has not been explicitly investigated so far. However, recent scanning tunneling microscopy experiments, focused on the study of acethylene adsorption on Si(111) surface,[15] revealed the appearance of a $\sqrt{3}$ periodicity. At first glance, in analogy with what was found for the other $\sqrt{3}$ systems just described, a naive interpretation would ascribe such reconstruction to C adsorption on the T_4 sites of the Si(111) surface. However, while Sn and Pb are immiscible in the bulk Si or Ge, C is not, so that the adsorption site determination can be more complicated. In order to deeply investigate this issue, we carried out a detailed total energy study of the C/Si(111) system, looking for the most stable adsorption sites and the possible occurrence of a 3×3 phase. Regarding the $\sqrt{3}$ phase, a similar calculation appeared recently in the literature;[16] their findings related to the structural, electronic, and energetic properties of this particular phase are in complete agreement with our present calculation.

We use the local density approximation to the density functional theory within the pseudopotential plane wave approach[17] to investigate this system. The Si(111) surface is modeled using a repeated supercell made of a three-bilayer slab. The bottom surface is saturated with hydrogens, while C adsorption is considered on different high symmetry sites at the top surface (see below for a more detailed discussion). Ultrasoft pseudopotential are used for C, Si, and H. A 25 Ry kinetic energy cutoff is found to be enough to achieve a well converged basis set; a 10×10 Monkorst-Pack shell is used for K-point sampling in the reduced Brillouin zone of the $\sqrt{3}$ unit cell. The atoms are let to relax towards their minimun energy configuration following the Hellmann-Feynman forces up to 10^{-2} eV/a.u.. In the $\sqrt{3}$ surface geometry, we considered the following C adsorption sites on Si(111): T_4, S_5, and H_3 (see Fig. 1).

The most energetically favored site is found to be the S_5 site; the energetically competing sites are the T_4 and H_3 sites, showing energies 1.3 and 2.0 eV higher than the S_5, respectively. A rationale for this finding can be found by looking at the different Si and C sizes; since C is smaller than Si, its
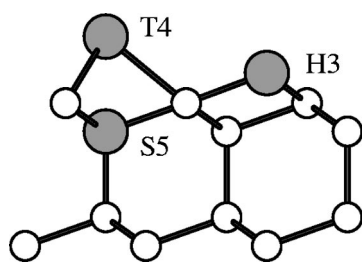
FIG. 1. Possible adsorption sites considered in the paper. For convenience, all the sites are represented in the same unit cell.

FIG. 3. Surface unit cell in the $\sqrt{3}$ and 3×3 phase. The large spheres represent the Si adatoms.

calculated equilibrium height on the T_4 site is only 0.61 Å, much smaller than the corresponding height for Si on T_4 (and C in S_5) (1.66 Å). As a result, the dangling bond energy is much higher for C than for Si.[18]

Looking in more detail at the structural properties of the C-covered fully relaxed $\sqrt{3}$, we find that the Si adatom–Si surface bond length is 2.42 Å, while the C–Si vertical bond (calculated between C in S_5 and the Si underneath) is 1.89 Å, much smaller than the ideal Si–Si bond length (2.35 Å) and very close to the Si–C bond length in SiC (1.88 Å). When C adsorbs on the T_4 site, the vertical bond length between the two Si atoms underneath is 2.25 Å. This evidentiates the nature of the surface state involved; it has antibonding character between the adatom and the Si underneath, while it has bonding character between the (111) subsurface A–Si bond[11,19] (A=Si or C). The population of the bonding state is mainly dictated by the adatom height.

The surface band structure is plotted in Fig. 2 for the most stable configuration found (C in S_5). We find that a surface state is cutting the Fermi level forming a surface localized band, mainly derived from the adatom Si p orbital, in the middle of the bulk band gap. This feature is similar to that found in all the other members of this class of surfaces.

Therefore, we investigate the occurrence of a possible structural distortion to the 3×3 phase. The relation between the $\sqrt{3}$ and the 3×3 surface unit cell is shown in Fig. 3.

To look for the equilibrium structure, we performed a constrained structural optimization, keeping fixed the surface
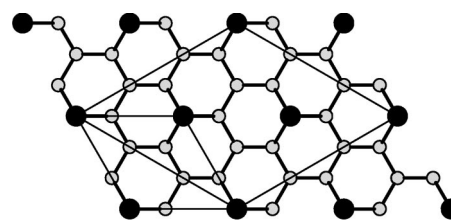
Si adatom relative height and letting all the other degree of freedom to relax. In this way we are exploring the potential energy surface along a particular $\mathbf{q}=\mathbf{K}$ ($\mathbf{K}$ being the high symmetry point of the surface Brillouin zone, see inset in Fig. 2) phonon coordinate of the $\sqrt{3}$ phase. The distortion was varied over a quite wide range of values, taking positive (1 Up–2 Down configuration) as well as negative values (2 Up–1 Down configuration). The total energy profile as a function of the rippling (i.e., the relative height) of the adatoms is shown in Fig. 4.

We find that the 3×3 phase has a lower total energy than the undistorted $\sqrt{3}$ structure, corresponding to a vanishing total distortion (Fig. 4). The system distorts in a symmetric way, showing a double minimum for positive and negative Δ ripple.[20] The energy gain (about 6 meV/adatom) and the total distortion (0.6 Å) are very similar in both 3×3 phases. Remarkably, the total energy gain is very similar to the Sn/Ge(111) case (9 meV/adatom), indicating that, if stable, the 3×3 phase should be observed at relative high temperature (liquid nitrogen). The occurrence of a double instability was never found in the other similar systems [Sn(Pb)/Ge(111)], where the observed distortion is of 1 Up–2 Down type, while for Sn/Si(111) was speculated to be the reversed one (2 Up–1 Down) due to the core-level spectroscopy evidences.[3,21]

The first proposed model for the structural instability of related systems was the CDW phase transition. The CDW is set up by the strong electron-phonon interaction and by the presence of a nested Fermi surface with a proper
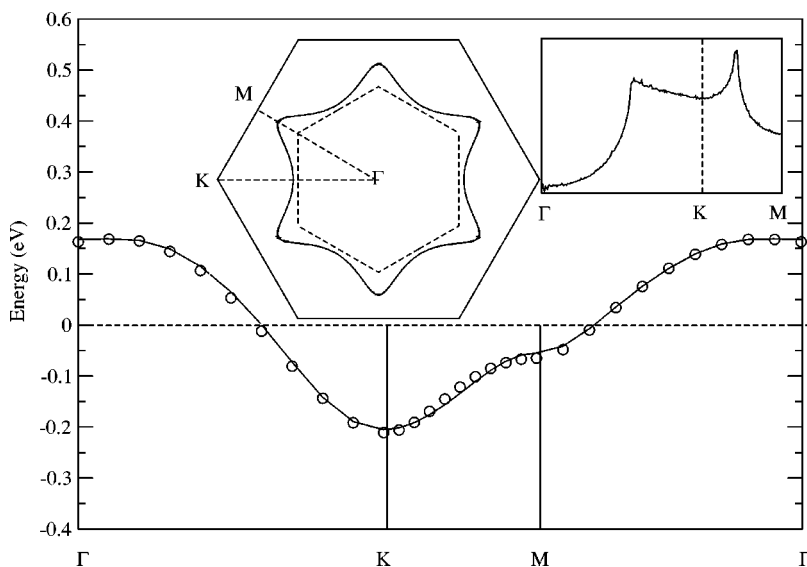

FIG. 2. Calculated surface band structure (circles) for C/Si(111) surface (with C occupying the S_5 site). The zero of the energy scale is set to the Fermi level. We report the adatom induced surface band. The solid line represents a tight binding fit of the *ab initio* energy band. The inset on the left represents the $\sqrt{3}$ (solid hexagon) and the 3×3 (dashed hexagon) surface Brillouin zone with the surface Fermi surface relative to the $\sqrt{3}$ phase (bold line). The inset on the right represents the zero-temperature Lindhard response function calulated for the $\sqrt{3}$ along the $\Gamma - K - M$ line.
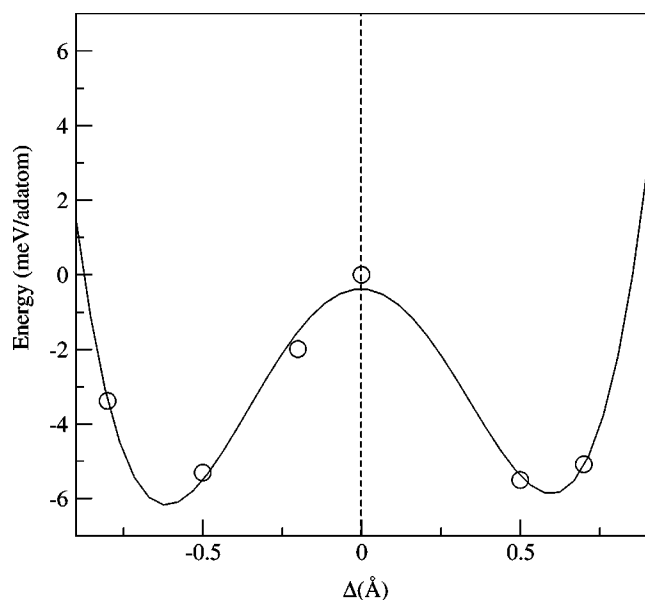
FIG. 4. Total energy (eV) as a function of adatom rippling (Å). Positive values represent the 1 Up–2 Down distortion, while negative values the 2 Up–1 Down distortion. The points are the calculated values, while the solid line represents a fourth-order polynomial fit.

wave vector. All the $\sqrt{3}$ surfaces of group IV metals on Ge and Si(111) surfaces do not present nesting at the 3×3 wave vector.[7] In order to look at the possible occurrence of a CDW phase, we calculate the Fermi surface of the $\sqrt{3}$ phase, performing a tight-binding fit of the surface band. As shown in Fig. 2 the calculated Fermi surface does not show any nesting; moreover, there is no particular feature in the calculated Lindhard response function at the **K** point. Thus, the occurrence of a CDW phase transition has to be ruled out.

Some important observations are relevant in this case: the band width of the surface state is 0.35 eV, smaller than in Sn(Pb)/Si(111) and Sn(Pb)/Ge(111) where it is found about 0.5 eV, much more similar to the SiC(0001) $\sqrt{3}$ case. This small bandwidth together with the high density of states at the Fermi level could, in principle, drive the system towards an electronic phase transition. In particular, it is possible to speculate that a Mott-Hubbard insulator phase can be reached, as predicted and observed in the case of SiC(0001) $\sqrt{3}$.[22,23] As a matter of fact, electron correlations effects are expected to play a crucial role in many of these systems. However, they are not as evident in Sn- and Pb-covered Ge(111) and Si(111). On the other hand, in SiC(0001), the situation is very favorable: here, there is a rather large band gap and a surface state with a pretty narrow bandwidth. It is therefore reasonable to expect an electronic phase transition to occur, as observed, even if no structural data are available to exclude some other structural phases. C/Si(111) seems very similar to the SiC surface, as far as the electronic properties are concerned; however, the occurrence of a structural deformation in the former makes this system more intriguing.

In conclusion, we report an *ab initio* study of the $\sqrt{3}$ phase of C adsorbed on the Si(111) surface. We found that the incorporation of C under the Si surface is energetically favorable. We predict the system to be unstable upon structural distortion towards a 3×3 structure, characterized by a double energy minimum along the $\mathbf{q}=\mathbf{K}$ phonon coordinate. We speculate that the study of C/Si(111) from both theoretical and experimental point of view can be very interesting, due to the possibility of the structural and electronic instabilities that may appear. New experiments and calculations are needed in order to gain more insights into the physics of this and other related surfaces.

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