Adsorption of acetylene on Si(100) is studied from first principles. We find that, among a number of possible adsorption configurations, the lowest-energy structure is a “bridge” configuration, where the C$_2$H$_2$ molecule is bonded to two Si atoms. Instead, “pedestal” configurations, recently proposed as the lowest-energy structures, are found to be much higher in energy and, therefore, can represent only metastable adsorption sites. We have calculated the surface formation energies for two different saturation coverages, namely 0.5 and 1 monolayer, both observed in experiments. We find that, in general, the full monolayer coverage is favored, although a narrow range of temperatures exists in which the 0.5 monolayer coverage is more stable, where the acetylene molecules are adsorbed in a 2×2 structure. This result disagrees with the conclusions of a recent study and represents a possible explanation of apparently controversial experimental findings. The crucial role played by the use of a gradient-corrected density functional is discussed. Finally, we study thermal decomposition of acetylene adsorbed on Si(100) by means of finite-temperature Molecular Dynamics, and we observe an unexpected behavior of dehydrogenated acetylene molecules.

I. INTRODUCTION

Adsorption of unsaturated hydrocarbon molecules on Si surfaces is of great importance to investigate the initial-stage growth of SiC films on Si substrates. In particular, there is an increasing interest in the study of adsorption of two basic hydrocarbon units, namely acetylene (C$_2$H$_2$) and ethylene (C$_2$H$_4$), on Si(100) surfaces.

Acetylene, due to its reactive triple bond, has a high probability of interacting with the surface Si dangling bonds, undergoing electronic rehybridization and sticking to the surface. Adsorption of acetylene on Si(100) represents a promising carbon source for homoepitaxial growth of cubic SiC because the processing temperature can be reduced well below 1000 °C, thus making it compatible with the present silicon technologies. In fact, at temperatures as high as 600 °C, acetylene already decomposes, leading to desorption of hydrogen and the formation of SiC clusters on the Si(100) surface. Furthermore, the diffusion of a small concentration of carbon atoms into the Si substrate may form a substochiometric alloy with interesting IR optical properties.

For the adsorption of acetylene on Si(100), as in the case of ethylene, most of the experimental and theoretical studies support the “di-σ” model, in which the acetylene molecule is adsorbed across a first-layer Si dimer in a bridge (B) site, with the Si dimers preserved (i.e. not cleaved) upon adsorption. Evidence favoring the B adsorption site comes from different experiments based on high-resolution electron-energy-loss spectroscopy, low-energy electron diffraction, X-ray photoemission spectroscopy, near-edge X-ray-adsorption fine structure, scanning tunnelling microscopy, photoelectron diffraction, and from theoretical calculations.

Recently, however, this scenario has been challenged by Xu et al. who studied the adsorption of ethylene and acetylene on the Si(100) surface by using a photoelectron holographic imaging technique. The most surprising result of this study was the observation of a new preferred adsorption site for acetylene on Si(100), where the molecule is bonded to four silicon atoms, in a pedestal configuration (P) between two adjacent Si dimers. This so-called “tetra-σ” model seems to be consistent also with high-resolution photoemission data.

By analyzing their diffraction images, Xu et al. infer a C-C distance in adsorbed acetylene of ∼1.2 Å. Even taking into account the indeterminacy associated to this
estimate (which, according to the authors, could be as large as 0.2 Å), this represents another surprising result. In fact this value is comparable with the experimental bond length of the triple C-C bond in the free acetylene molecule (1.21 Å), whereas, for the sp²-hybridized acetylene adsorbed in the P site, one would expect a much longer bond, close to the single C-C bond of, say, C₂H₆ (1.54 Å).

Another somewhat controversial issue concerns the C₂H₂ equilibrium coverage which is most likely to be realized on the Si surface. Based on experimental measurements, both 0.5 monolayer (ML) and 1 ML coverages have been proposed as saturation coverages realized, in equilibrium conditions, on the Si(100) surface (1 ML means that as many C₂H₂ molecules are adsorbed as Si surface dimers). In particular, STM experiments performed at room temperature indicated[8] that the C₂H₂ molecules form a local p(2 × 2) or c(4 × 2) structure with a saturation coverage of 0.5 ML. Detailed analysis of the STM images reveals lack of adsorption on nearest-neighbor sites, thus showing that the C₂H₂ molecules adsorb on alternate dimers: the two observed surface periodicities depend on whether the C₂H₂ molecules adsorbed on adjacent rows are in phase or out of phase. On the other hand kinetic uptake measurements[22] performed at lower temperatures (105 K), provide evidence for 1 ML coverage, i.e. each Si dimer site adsorbs a single C₂H₂ molecule. These different experimental observations have been tentatively explained[19] by assuming that the early stages of acetylene chemisorption are kinetically rather than thermodynamically driven, i.e. adsorption proceeds via precursor states[19] which although not truly thermodynamically stable states, are separated by sizeable potential barrier from the stable adsorption configurations.

The process of thermal desorption of acetylene on Si(100) is also of interest. It has been found[20] that, as the surface temperature is raised up to 870 K, the acetylene molecules dissociate, leading to the formation of SiH groups and surface carbon. However, the details of the dissociation paths and the early stages of surface carbonization are not known. Simulations performed using ab-initio finite-temperature Molecular Dynamics can provide valuable information to elucidate such complex phenomena.

In order to clarify the above issues, we have performed a full ab initio study of acetylene adsorption on Si(100), by using the Car-Parrinello approach.[23]

The paper is organized as follows. In Section II we describe the computational method. We report our results for the adsorption geometries, with particular emphasis on the energetic and structural characterization of the B and P configurations, in Section IIIA. In Section IIIB we address the problem of the theoretical determination of the C₂H₂ equilibrium coverage. Our calculations of the surface formation energies for different model structures at 0.5 and 1 ML coverage provide evidence that the saturation coverage depends on temperature, largely favoring the 1 ML coverage, but indicating the existence, for a particular adsorption configuration, of a narrow window in temperature (which we find only qualitatively in agreement with the experiment), where the 0.5 ML coverage may become favored. We offer this prediction, which disagrees with the conclusions of Ref. [3], as a semi-quantitative explanation for the different experimental observations quoted above.

Finally, in Section IV we present the results of our simulations of thermal dissociation of C₂H₂ on Si(100); this is a very important topic being related with the process of growth of SiC films obtained from decomposition of acetylene chemisorbed on the Si(100) surface. Our results are encouraging and show some interesting behavior, including a tendency of the acetylene molecules to decompose into intact C dimers, which diffuse below the Si surface layer and bind themselves to form more complex structures.

II. METHOD

Total-energy calculations and Molecular Dynamics (MD) simulations have been carried out within the Car-Parrinello approach[22] in the framework of the density functional theory, both in the local spin density approximation (LSDA) and using gradient corrections in the BLYP implementation[24]. Gradient-corrected functionals have been adopted in the most recent theoretical studies of adsorption of organic molecules on Si(100) because they are typically more accurate than the LSDA functional in describing chemical processes on the Si(100) surface[24]. The calculations have been carried out considering the Γ-point only of the Brillouin zone (BZ), and using norm-conserving pseudopotentials[25] with s and p nonlocality for C and Si. Wavefunctions were expanded in plane waves with an energy cutoff of 50 Ry. We have explicitly checked that, at this value of the energy cutoff, the structural and binding properties of our system are well converged.

In order to test the above approximations, we have calculated the structural and vibrational properties of the free acetylene molecule (see Table 1) and find an excellent agreement with the experimental estimates and previous theoretical calculations[26].

The Si(100) surface is modeled with a periodically repeated slab of 5 Si layers and a vacuum region of 7 Å (tests have been also carried out with a vacuum region of 10 Å, without any significant change in the results). A monolayer of hydrogen atoms is used to saturate the dangling bonds on the lower surface of the slab. We have used a p(4 × 4) surface supercell in the (2 × 1) reconstruction, corresponding to 16 Si atoms/layer (some calculations have been performed using instead a (4 × 2) reconstruction, see Section IIIB). With such a relatively large supercell we expect that a sampling of the BZ limited to the Γ point is adequate. A sensitive test for the ade-
quacy of the $k$-point sampling is provided by the study of the clean Si(100) surface: as discussed below, the correct surface structure is obtained with our supercell.

Structural relaxations of the ionic coordinates are performed using the method of direct inversion in the iterative subspace. During ionic relaxations and MD simulations the lowest Si layer and the saturation hydrogens are kept fixed. We verified that, by starting with the un-reconstructed, clean Si(100) surface, the structural optimization procedure correctly produces asymmetric surface dimers, with a dimer bond length and buckling angle in good agreement with previous, highly converged ab initio calculations. Acetylene molecules are added on top of the slab and the system is then fully relaxed towards the minimum energy configuration. To better explore the complex potential energy surface of this system, in most of the cases the optimization procedure was repeated using a simulated-annealing strategy and also starting from different initial configurations. The same optimization procedure has been already successfully applied to the study of adsorption of benzene on Si(100).

Among the many possible adsorption configurations for acetylene on Si(100) we have focused our study on the B and P structures (those involved in the present controversy about the lowest-energy site), although calculations have been performed for other configurations as well. Adsorption of acetylene between two adjacent dimer rows is not considered in our calculations, since it is known to result in structures having much lower binding energies.

### III. RESULTS

#### A. Lowest-energy adsorption sites

Four possible configurations of acetylene adsorbed on Si(100) are shown in Fig. 1. The energetics and the structural properties are summarized in Table II. When comparing the total energies of different adsorption configurations, we consider a representative 0.5 ML coverage of acetylene on Si(100), corresponding to two Si dimers per $\text{C}_2\text{H}_2$ molecule. This is the coverage realized in the experiments by Xu et al. and the one which is likely to be prevailing at room temperature. Note that calculations performed at lower coverage (for instance at 0.125 ML coverage, corresponding, in our supercell, to a single acetylene molecule adsorbed on the slab) do not alter the conclusions contained in Table II as far as the energetic ordering of the structures is concerned.

We confirm that both the P and B structure are possible adsorption configurations, and that the Si dimers involved in bonding with acetylene are preserved (in line with the most recent experimental and theoretical works, see Refs. 9, 11 and further references quoted therein), although the typical buckling of the (2×1) reconstruction is removed and the Si dimers become symmetric (this latter result is also in agreement with previous calculations, see, for instance, Ref. 10). According to our data the P structure, however, lies at much higher energy than the B one. Interestingly, a lower-energy pedestal configuration (P') is obtained by rotating the P structure by 90° with respect to the Si surface. In this configuration, the four C-Si bonds are shorter than in the P one. However, P' is also found to be less favored than B. If the B structure is rotated by 90°, in such a way to bridge two Si atoms of two adjacent dimers, one obtains another possible adsorption configuration, B', slightly higher in energy than B. Our results compare favorably with those of the recent paper by Sorescu and Jordan, where however the adsorption energies for the B and B' structures at 0.5 ML coverage are not reported. We also find that, at higher coverage, the B' structure becomes favored with respect to the B one (the energy difference is ~ 0.14 and 0.19 eV/molecule, using the LSDA and BLYP functional, respectively), again in agreement with the calculations of Sorescu and Jordan.

As can be seen in Table II, use of BLYP gradient corrections instead of LSDA makes bond lengths about 1-2 % longer; moreover the P' configuration is much less energetically favored, and the B and B' structures are almost degenerate. Note however that the energetic ordering of the four different structures remains unchanged.

Our results contradict the findings of Xu et al. that the P site is the stable adsorption site, and confirm instead the conclusions reported in the previous literature. For the B configuration, which is certainly the favored one at coverages not higher than 0.5 ML, our structural parameters are in excellent agreement both with the experimental estimates of Matsui et al. (C-C bond length=1.36 ± 0.04 Å) and Terborg et al. (C-C bond length=1.36 ± 0.19 Å, C-Si bond length=1.83 ± 0.04 Å) and with the most recent theoretical calculations. In the B structure our optimized C-C bond length (1.35-1.36 Å) is close to that of ethylene (1.33 Å), suggesting $sp^2$ rehybridization of the C-C bond. $sp^2$ bonding is supported by Imamura et al. who reported charge-density plots where the characteristic $\pi$-bonds are observed, and by Matsui et al. who observe $\pi^*$ features in near edge X-ray adsorption fine structure spectra. Our computed vibrational frequency of the C-C stretching mode is 1440 cm$^{-1}$, which compares favorably both with the experimental value of Huang et al. (estimated to be in the range 1450-1500 cm$^{-1}$) and with the previous ab-initio estimate by Imamura et al. (1479 cm$^{-1}$).

Note that, as expected, the C-C bond length in the P and P' structures is significantly larger than in the B one, and is not consistent with the value, 1.2 ± 0.2 Å, observed by Xu et al. This leads to the conclusion that, either the experimental indeterminacy associated to the C-C bond length is largely underestimated, or the structure observed by Xu et al. is not a pedestal one.

For the B structure, again at 0.5 ML coverage, our
computed adsorption energy (78 kcal/mol using LSDA, 65 kcal/mol with BLYP) is in good agreement with previous theoretical estimates [12, 13] (ranging from 55 to 77 kcal/mol). The substantial energy difference between the bridge (B, B') structures and the pedestal (P, P') ones strongly supports the conclusion that the bridge adsorption sites are the stable configuration for acetylene on Si(100), while the pedestal structures can represent only metastable adsorption sites.

Other possible adsorption structures exist, besides those shown in Fig. 2 (see also Ref. 19). For instance, we found a “diagonal-bridge” (DB) configuration in which the acetylene molecule forms a cross-bridge structure with two Si atoms belonging to two neighbour Si dimers of the same row. This configuration can occur as one considers reconstructions of the Si surface involving alternating buckled Si dimers, such as the p(2×2) and the c(4×2). However, according both to our calculations and to those of Sorescu and Jordan [20], the DB structure is even energetically less favored than the P' one.

### B. Saturation Coverage

Having assessed the quality of our approach by comparing our structural and energetical data with previous theoretical and experimental studies, we are now in the position to deal with the issue of saturation coverage, where a high accuracy is essential to get meaningful information.

STM measurements [18, 19] of C$_2$H$_2$ on Si(100), performed at room temperature, indicate a saturation coverage of 0.5 ML (one acetylene molecule adsorbed every two Si surface dimers). However, other experimental measurements [4] suggest instead a saturation coverage of 1.0 ML. We show in the following that, although the 1.0 ML coverage seems to be generally preferred, in principle both coverages can be realized depending on the temperature of C$_2$H$_2$ deposition and on the adsorption configuration.

The 0.5 ML coverage can be realized in a number of ways, even assuming that each of the acetylene molecule is adsorbed in the lowest energy structure, i.e. the B structure (see Fig. 2). In particular, as shown in the following, the relative energy ordering is influenced by the structure of the Si dimers which are not saturated by C$_2$H$_2$ molecules. These may be characterized by a different relative buckling orientation. Here we adopt the same notation used in Ref. 18 to identify these different structures. The full monolayer (1 ML) coverage, on the contrary, is compatible only with a single configuration if the acetylene molecules are adsorbed in the B structure.

Using first-principles calculations Tanida et al. [18] predict, for the most stable 0.5 ML coverage structure, one (structure (a) in Fig. 2) where alternated dimer rows are fully covered with C$_2$H$_2$ molecules. However such structure is not compatible with the STM observations of Ref. 18 performed at room temperature. According to these observations, at 0.5 ML coverage the acetylene molecules are instead adsorbed on alternate dimers in the same rows, and on adjacent rows they can be in phase or out of phase. Note that instead the (c)-(f) configurations, which are characterized by (2×2) or (4×2) periodicity, are all compatible with the STM observations of Ref. 18.

Using the BLYP functional we confirm (see Table II) the result of Ref. 18 that the (a) structure is at the lowest energy. However, at variance with Ref. 18, we find that the (a), (c), and (e) structures are almost degenerate in energy. This discrepancy could be due to the fact that Tanida et al. [18] use a smaller cell than ours and possibly to the different gradient-corrected functional they adopt. Note that in this case the effect of the gradient corrections is not a simple quantitative correction to the LSDA results; in fact using the BLYP functional the energetic ordering of the different configurations is completely changed (see Table II).

At thermal equilibrium the optimal surface structure can be determined by computing the grand canonical potential. We show in Fig. 3, for the structures (a) and (e) of Fig. 2, the behavior of ∆Ω, that is the difference between the grand canonical potential of a given structure and that of the clean Si(100) surface. ∆Ω is defined as

\[
\Delta \Omega = \Delta E - N_{C_2H_2} \mu_{C_2H_2},
\]

where \(\Delta E\) is the difference between the total energy of the considered structure and that of the clean Si(100) surface (using the lowest-energy surface reconstruction which is compatible with the given configuration, that is (4×2) for configuration (a) and (2×1) for configuration (e), respectively), and \(N_{C_2H_2}\) is the number of the C$_2$H$_2$ molecules; following Ref. 18 the zero of the chemical potential \(\mu_{C_2H_2}\) is assumed to be 1/3 of the energy of the isolated benzene (C$_6$H$_6$) molecule in vacuum. Calculations were performed using the BLYP gradient-corrected functional. As can be seen, for structure (a) the preferred saturation coverage appears to be 1.0 ML, in agreement with the findings of Tanida et al. [18] and the same is true for the structures (b), (c), (d), and (f) (the corresponding \(\Delta \Omega(\mu_{C_2H_2})\) curves are not shown because they closely resemble those of structure (a)). However, in the configuration (e), there is instead a range of values of the chemical potential for which the 0.5 ML saturation coverage becomes favored. Note that, considering the adsorption structure B' in place of B, the 1.0 ML saturation coverage would be always favored, since this structure is the preferred one at high coverage (see previous discussion).

Configuration (e), with a 2×2 periodicity, is compatible with STM measurements at room temperature and, according to our calculations (see Table II), is also one of the lowest-energy configurations at zero temperature, being almost degenerate with configuration (a); since it is the only structure for which the 0.5 ML coverage could be favored instead of the 1.0 ML coverage, we have tried
to estimate in which range of temperatures this particular configuration is stable. To this aim we have followed the procedure described in Ref. 33. The surface formation energy, whose minimum determines the equilibrium state of the surface as a function of composition, is defined as $\Omega/A$, $A$ being the surface area and

$$\Omega(T) = F - \sum_i N_i \mu_i$$  \hspace{1cm} (2)

is the grand canonical potential (we have omitted a $PV$ term which, for the pressures considered here, is negligible). $F$ is the free energy of the system, $N_i$ is the number of particles of type $i$, and $\mu_i$ denote the chemical potentials of the various components. If one assumes that the Si(100) surface is in equilibrium with bulk Si (this is the natural reservoir for Si atoms, due to the presence of steps, terraces and other surface defects), then for the bare Si(100) surface one has:

$$\Omega_{\text{bare}} = E[\text{Si}(100)] - N_{\text{Si}} E_{\text{bulk}}[\text{Si}]$$  \hspace{1cm} (3)

where the first term is the total energy of the slab and the second term is the energy per atom of bulk Si multiplied by the total number of Si atoms of the cell. In the above expression the temperature dependence of the free energy of the slab and that of the bulk reservoir have been neglected, as usually done in this kind of calculations. The formation energy of the acetylene-covered surface can be estimated, following the same reasoning, by computing

$$\Omega(T) = E[\text{Si}(100)]:\text{C}_2\text{H}_2] - N_{\text{Si}} E_{\text{bulk}}[\text{Si}] - N_{\text{C}_2\text{H}_2} \mu_{\text{C}_2\text{H}_2}(T) +$$

$$+ F_{\text{ads}}$$  \hspace{1cm} (4)

where $F_{\text{ads}}$ is the free-energy contribution due to the vibrations of the adsorbed $\text{C}_2\text{H}_2$ molecules. In order to estimate the temperature dependence of $\mu_{\text{C}_2\text{H}_2}$ we assume, quite reasonably, that the surface is in equilibrium with a reservoir of acetylene molecules in the gas phase. Therefore, using elementary statistical mechanics,

$$\mu_{\text{C}_2\text{H}_2}(T) = E_{\text{C}_2\text{H}_2} + kT \ln(PV/Q/kT) - kT \ln Z_{\text{rot}} - kT \ln Z_{\text{vib}}$$  \hspace{1cm} (5)

Here $E_{\text{C}_2\text{H}_2}$ is the total energy of the isolated acetylene molecule, $P$ is the pressure, and $Q = (h^2/2\pi mkT)^{3/2}$ is the quantum volume. The rotational and vibrational contribution to the chemical potential are calculated using the experimental values of the vibrational frequencies for the free acetylene molecule. We estimate the pressure $P$ from realistic growth conditions of $\text{C}_2\text{H}_2$ films on Si(100): experimentally, the saturation coverage is realized under an acetylene exposure of $\sim 2$ L, which corresponds to $P \approx 2 \times 10^{-6}$ Torr. The vibrational contribution $F_{\text{vib}}(T) = \sum_i [\hbar \omega_i/2 + kT \ln(1 - \exp(-\hbar \omega_i/kT))]$ is estimated from the vibrational frequencies calculated in Ref. 10 (the frequencies of the hindered modes $T_x$, $T_y$ and $R_z$, which are not included among the mode frequencies reported in Ref. 10, have been estimated here by using a “frozen-phonon” approach).

Our calculations show that, in the temperature range from 410 to 460 K, the adsorption configuration (e) at 0.5 ML coverage is energetically favored with respect to that corresponding to 1 ML coverage. Since this temperature interval is not far from room temperature (given the approximations involved in our derivation the accuracy of our temperature estimate is of course limited) we conclude that configuration (e) could be realized as a stable adsorption configuration at room temperature. This result, which disagrees with the conclusions of Tanida et al. (according to Ref. 33 the 0.5 ML coverage is never favored), is in qualitative agreement with the experimental observation that full monolayer coverage is realized at $T = 105$ K, while the 0.5 coverage is observed in STM experiments performed at room temperature. Of course this does not rule out the possibility that the existence of precursor states could play a crucial role in destabilizing the surface species for coverages greater than 0.5 ML; however it offers an alternative/complementary explanation of the experimental findings.

C. Thermal decomposition of $\text{C}_2\text{H}_2$ on Si(100)

As a result of the high desorption activation energy of $\text{C}_2\text{H}_2$ on Si(100), adsorbed acetylene molecules tend to be retained on the surface up to relatively high temperatures. According to the EELS and LEED measurements of Nishijima et al. upon heating the $\text{C}_2\text{H}_2$-exposed Si(100) surface from 80 up to 750 K, the C-H bond scission occurs, with a gradual recombination of the dissociated H atoms onto the Si(100) surface; the C-C bond scission takes place by further heating the sample at 870 K, while by heating up to 930 K the surface hydrogen is probably completely removed by H$_2$ desorption; similar qualitative results have been obtained in theoretical calculations by Zhou et al.

The proposed decomposition path is therefore: $\text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_x (x=0,1) \rightarrow \text{C} + \beta$-SiC; the activation barrier for the dissociation of a single H atom is estimated to be no less than 0.8 eV, while that for the the dissociation of the remaining C$_2$ species is about 1.3 eV. This indicates that acetylene favors dehydrogenation to C$_2$H$_x$ (x=0,1) species first; then the remaining C$_2$ dimers further decompose into C$_x$ species to form $\beta$-SiC films. However it is not at all clear if, after acetylene dehydrogenation, all the H atoms desorb as a gas of H$_2$ molecules or if instead some of them actually form Si-H bonds. Also the weakening of the Si dimer bonds, as a consequence of heating the sample, could be relevant: according to Imaiura et al. although the dimerized structure is more stable than the dimer-cleaved one, the latter structure may be taken instantaneously just after the adsorption, and the Si-Si bond-breaking and rebonding oscillations could occur at relatively high temperatures. Finally, in view of the SiC-growth characterization, it would be very interesting to clarify how, after acetylene dissociation,
carbon atoms diffuse into the bulk of the Si crystal.

We have performed Car-Parrinello MD simulations at finite temperature in order to investigate the dissociation of acetylene on Si(100). The ionic degrees of freedom have been integrated using a time step of 5 a.u. (∼0.12 fs) and typical MD runs were 3-4 ps long. We start with a configuration where the C$_2$H$_2$ molecules are adsorbed on the Si(100)$(2 \times 1)$ surface in the B structure at 0.5 ML coverage. The initial geometry is optimized using the method described in Section II. We gradually heat this structure by simply rescaling the ionic velocities. Obviously we are forced to use heating rates much higher than in actual experiments in order to let the system undergo some kind of transformations; this however would lead to melting of the whole sample prior to C$_2$H$_2$ desorption/decomposition. In order to overcome this unphysical effect, we have adopted a simple z-dependent heating scheme, in which the temperature decreases as one moves towards the interior of the slab. In this way the adsorbed acetylene molecules and the uppermost Si atoms are kept at higher temperatures than the remaining ions, thus avoiding melting of the whole slab. Although both in the simulations and in actual experiments the details of the heating procedure may significantly affect the final system configuration, we believe that our scheme is able to reproduce, at least at a qualitative level, the basic features of the desorption process.

The main results of our MD simulations can be summarized as follows (given the heating procedure followed, our “simulation temperature” is not particularly meaningful for comparison with the experimental one): 1) by heating the sample the first relevant event is the dissociation of some C-H bonds (typically one H atom is detached from every molecule); 2) then C-Si bonds are continuously broken and reformed leading to diffusion of the acetylene molecules on the Si surface; 3) by further increase in the temperature, some C$_2$H$_2$ molecules loose their H atoms, remaining on the surface as C-C dimers; 4) these dimers remain intact even at very high temperatures; 5) the dissociated H atoms prefer to form new bonds with Si atoms rather than forming H$_2$ molecules, although in our simulation this tendency could be enhanced by the finite size of the vacuum region; 6) the C-C dimers eventually form complex sub-surface structures, just below the first Si layer, such as a 5-atom ring composed by one Si atom and 4 C atoms.

Some of the above results are consistent with experimental observations. In fact, in the early stages of annealing, a strong Si-H stretching mode is visible in the HREELS spectrum, thus supporting the formation of Si-H bonds, while the peak due to C-C stretching broadens and develops a long tail; this latter result could indicate that breaking of C-C dimers could be only partial or/and much slower than H dissociation. The surprising stability of C-C dimers has been confirmed by using different heating rates and also adopting the LSDA functional instead of BLYP. This remarkable effect is in contrast with previously proposed desorption mechanisms which just assume a simple C-C dimer thermal breaking (see for instance Ref. [1]). Note that the same result has been obtained by Cicero et al. from simulations in which they studied the heating of carbon dimers adsorbed on Si(100).

This however poses the problem of how SiC (whose formation is believed to require breaking of C-C dimers) is actually produced. A possible explanation could be the presence, in real experiments, of a gas of silanes (such as Si$_2$H$_6$) which could play a crucial role in the SiC growth: in fact adsorbed Si atoms can react with the C$_2$H$_2$ molecules, and C-C dimer breaking could actually occur before acetylene adsorption.

IV. CONCLUSIONS

Adsorption of acetylene on Si(100) has been investigated using ab initio simulations. The structural and energetic properties of possible adsorption configurations have been studied. Although the P structure, recently suggested by Xu et al. as the lowest-energy configuration, is found to be stable, our results show that the bridge structures (B or B’, depending on the coverage) are energetically favored, in agreement with most of the previous studies. The results reported by Xu et al. could be influenced by the presence of defects, such as steps, which could make the actual Si surface used in their experiment substantially different from the ideal Si(100) surface assumed (see Fig. 2 of Ref. [20]) in the interpretation of the experimental data.

We have then addressed the issue of the saturation coverage and its dependence on the temperature, and we find that, although the full monolayer coverage is generally preferred, there is a temperature window, not far from room temperature, in which a particular adsorption structure at 0.5 ML coverage is preferred. This could explain the results of STM observations performed at room temperature. The effects of including gradient corrections have been also discussed: our calculations show that these effects are particularly relevant for the determination of the optimal adsorption configuration at 0.5 ML coverage, where even fine structural details, such as the relative orientation of the buckled Si-dimers, may be important for the correct determination of the surface formation energies.

Finally we have reported the results of our MD simulations of the thermal decomposition process of acetylene molecules on Si(100); in particular we observe a surprising stability of the (dehydrogenated) C dimers and their tendency to diffuse below the first Si layer and to coalesce into more complex C fragments.
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FIG. 1. Stable structures of acetylene adsorbed on Si(100), in the (2 × 1) reconstruction: B="bridge", B’="rotated bridge", P="pedestal", P’="rotated pedestal". For clarity only the four Si atoms of two dimers and four belonging to the second layer are shown.

FIG. 2. Different possible structures of acetylene adsorbed on Si(100) in the B configuration, at 0.5 ML coverage: up atoms of Si dimers are indicated by solid circles, down atoms of Si dimers (and those belonging to symmetrized Si dimers) by open circles, and adsorbed acetylene molecules by solid bars.

FIG. 3. Grand canonical potential for the Si(100)-C$_2$H$_2$ surface at zero temperature, as a function of the chemical potential $\mu$C$_2$H$_2$, for the structures (a) and (e) shown in Fig. 2, at 0.5 ML coverage (dashed line); data are compared with those obtained at 1.0 ML coverage (solid line). The values are relative to the grand canonical potential of the clean Si(100) surface (horizontal line).

TABLE I. Bond length distances and vibrational frequencies of the free acetylene molecule. For comparison, besides the experimental values, we also report the LSDA results from Ref. 26 (in parenthesis).

|                  | LSDA  | BLYP  | expt. |
|------------------|-------|-------|-------|
| C-C (Å)          | 1.201 | 1.206 | 1.203 |
| C-H (Å)          | 1.075 | 1.066 | 1.061 |
| C-H stretching (cm$^{-1}$) | 3304  | 3337  | 3374  |
| C-C stretching (cm$^{-1}$) | 1975  | 1960  | 1974  |
| C-H bending (cm$^{-1}$)  | 739   | 743   | 729   |

TABLE II. Total energy per adsorbed molecule (relative to the B structure), $E$, and structural parameters for acetylene on Si(100), at the saturation coverage of 0.5 ML. “Si” indicates the silicon atoms involved in bonding with acetylene. Data have been computed using the gradient-corrected BLYP (Ref. 23) functional. Values obtained using the LSDA functional are instead reported in parenthesis. When slightly different distances are found the average value is given. See text for the definitions of the different structures.

| Configuration | $E$(eV) | $d_{C-C}$(Å) | $d_{C-Si}$(Å) | $d_{Si-Si}$(Å) |
|---------------|---------|--------------|---------------|---------------|
| B             | 0.00    | 1.36 (1.35)  | 1.91 (1.88)   | 2.37 (2.34)   |
| B’            | 0.05 (0.27) | 1.37 (1.36) | 1.92 (1.89)   | 2.43 (2.36)   |
| P             | 1.98 (1.94) | 1.58 (1.54) | 2.07 (2.02)   | 2.37 (2.33)   |
| P’            | 1.28 (0.53) | 1.57 (1.53) | 2.01 (1.96)   | 2.32 (2.28)   |

TABLE III. Total energy (in meV) per adsorbed molecule (relative to the (a) structure) for different structures of acetylene adsorbed on Si(100) in the B configuration (see Fig. 2), at 0.5 ML coverage and zero temperature, obtained using the LSDA and BLYP functional, respectively.

| Configuration | LSDA | BLYP |
|---------------|------|------|
| (a)           | 0    | 0    |
| (b)           | -21  | 89   |
| (c)           | -35  | 2    |
| (d)           | -22  | 18   |
| (e)           | -31  | 3    |
| (f)           | -26  | 17   |
Chemical potential (eV)

Grand canonical potential (eV/dimer)

Chemical potential (eV)