

## Ab initio investigation of the adsorption of organic molecules at Si(1 1 1) and Si(1 0 0) surfaces

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### Abstract

To investigate the early stages of SiC growth on silicon, we performed an ab initio study of the adsorption of C<sub>2</sub>H<sub>2</sub> and other small organic molecules on different Si surfaces. Our calculations, based both on geometry optimization and on finite-temperature molecular dynamics simulations, show that for all the molecules that we have considered the preferred adsorption sites at low temperature are confined at the surface, with no sub-surface penetration. Adsorption occurs through the formation of Si–C bonds, accompanied by a distortion of the adsorbed molecule to adapt the Si–C distance to the SiC bulk bond length. We discuss similarities and differences upon changing the organic molecule and the crystal face. To complete the study with the computation of directly measurable quantities, we analyze the optical reflectance anisotropy of one simulated structure.

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### 1. Introduction

The adsorption of small organic molecules, such as acetylene, benzene, ethylene and also methylsilane, on semiconductor surfaces, is currently the object of several experimental and theoretical investigations. These molecules are interesting precursors suitable for the low temperature growth of SiC on Si substrates [1,2]. The microscopic features of the growth process are still

unknown, and there are controversies about the adsorption sites and about the nature of the bond between the C atoms of the molecules and the Si surface atoms [3].

To get insight into this problem, we performed ab initio calculations for the adsorption of acetylene [4] on the Si(1 0 0)-2×1 and on the Si(1 1 1)-2×2 surfaces, and for the adsorption of methylsilane on the Si(1 0 0)-2×1 surface only. The Si(1 1 1)-2×2 surface was considered as a reduced model of the relevant portion of the Si(1 1 1)-7×7 reconstruction. In fact, high resolution electron energy loss spectroscopy (HREELS) experiments indicate that C<sub>2</sub>H<sub>2</sub> molecules adsorb in a bridge

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configuration between the rest-atom and the ad-atom of the Si(1 1 1)- $7\times 7$  surface [5]. This limited part of the reconstruction, that is supposed [5] to be mostly involved in the chemisorption, may be modeled with a  $2\times 2$  surface periodicity.

The two different crystal faces that we took into account offer different scenarios to the impacting molecules, and therefore the choice of one surface rather than the other may facilitate or hinder the growth of SiC. For instance, the (1 0 0) surface termination is characterized by Si–Si dimers, and a foreign molecule may adsorb either on a dimer or between two dimers, whereas adsorption on top of Si atoms is expected to be highly unfavorable. The stable (1 1 1) surface termination exhibits instead ad-atoms, rest-atoms, stacking faults, and vacancies: on the basis of symmetries, the expected locations for molecular chemisorption are around Si vacancies, on the rest-atom (ad-atom), or bridging the ad-atom and the rest-atom. In our simulations we took into account only the latter condition. In this paper, we present the first-principle results about the structural stability, and discuss them in terms of differences and similarities in SiC growth depending on the choice of the molecular precursor and of the substrate orientation.

## 2. Method

Our calculations were performed in the frame of the density functional theory and in the pseudo-potential approach. All the atomic species were treated by norm-conserving Troullier–Martins pseudopotentials generated consistently with the BLYP [6] parameterization of the exchange–correlation functional. The electronic states were expanded in a plane wave basis set with a kinetic energy cutoff of 50 Ry.

The surfaces were represented by periodically repeated supercells, including a thick vacuum region to inhibit the interaction between the opposite surfaces of a slab and between replicas. For both the (1 0 0) and (1 1 1) orientations, one surface of the slab was terminated by a complete H monolayer to saturate the dangling bonds of the silicon atoms and preserve the bulk configuration. The Si(1 0 0)- $2\times 1$  surface was modeled with a su-

percell having a  $p(4\times 4)$  periodicity, and containing 6 Si layers and 7 Å of vacuum. Only the  $\Gamma$  point was considered in Brillouin-zone (BZ) sums, and the convergence was tested as a function of the lateral extension of the supercell. The Si(1 1 1)- $2\times 2$  surface was modeled with a supercell having a  $2\times 2$  periodicity, and containing 6 Si bilayers, one Si ad-atom per cell, and 11 Å of vacuum. The BZ sums were performed on a uniform Monkhorst–Pack grid including two special  $k$  points in the irreducible part of the BZ.

## 3. Results and discussion

A detailed account of the adsorption of acetylene on the Si(1 0 0) surface is reported elsewhere [4]. Here, we summarize the main results to allow for a direct comparison with the investigation of the (1 1 1) crystal face, and to discuss the efficiency of  $C_2H_2$  as a precursor for the growth of SiC.

Several metastable equilibrium configurations ( $T = 0$  K) were found for  $C_2H_2$  on Si(1 0 0) in the 0.5 ML coverage regime (1 acetylene molecule every two surface Si dimers): in Fig. 1, the most stable structures are illustrated in a  $2\times 2$  portion of the

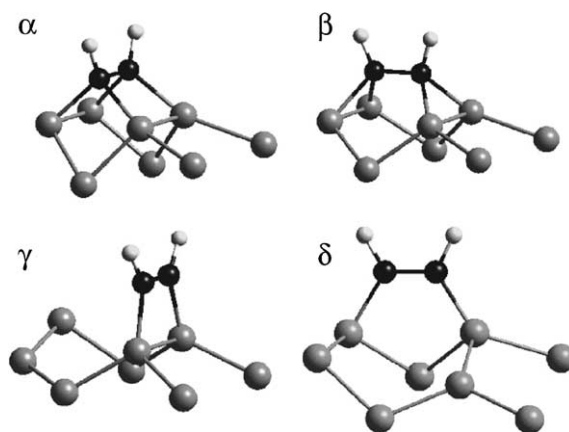


Fig. 1. Stable configurations for the adsorption of  $C_2H_2$  on the Si(1 0 0)- $2\times 1$  surface. “ $\gamma$ ” is the most stable one, almost degenerate with “ $\delta$ ”. Configurations “ $\alpha$ ” and “ $\beta$ ” are characterized by single C–C bonding, “ $\gamma$ ” and “ $\delta$ ” by double C–C bonding.

$p(4\times 4)$  cell. The  $\alpha$  configuration is characterized by the adsorption of  $C_2H_2$  parallel to the Si surface dimers, each C atom of the molecule is bonded to two surface Si atoms belonging to two different dimers. The  $\beta$  configuration is obtained by a  $90^\circ$  rotation: each C atom of the molecule is bonded to the two Si atoms that form a dimer. Configurations  $\gamma$  and  $\delta$  are characterized by single bonding of the C atoms to surface Si atoms, of the same dimer and of two different dimers, respectively. The energy gain per molecule, due to adsorption, is respectively 0.85, 1.55, 2.85, and 2.84 eV, for the structures  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ . This energy ordering indicates that  $\gamma$  is the most stable configuration among those considered, and  $\delta$  is almost degenerate with  $\gamma$ . It is important to note that for the structures  $\alpha$  and  $\beta$  the C–C distance is 1.56 Å, characteristic of single bonding; instead, for the other two structures  $\alpha$  and  $\beta$ , the C–C distance is 1.36 Å (as in the case of the ethylene molecule), indicating a double bond within the C dimer. The double bonding of the carbon dimer is confirmed by the frequency of the C–C stretching mode: by means of a frozen phonon calculation, we found a frequency of  $1440\text{ cm}^{-1}$  in good agreement with experimental findings [7].

The above results show that  $C_2H_2$  molecules preferentially adsorb on top of the dimers ( $\gamma$  configuration) of the  $Si(100)\text{-}2\times 1$  surface, in the 0.5 ML coverage. However, this may be accomplished in several inequivalent ways (see Fig. 2). In particular, the relative energy ordering is influenced by the structure of the Si dimers which are not saturated by  $C_2H_2$  molecules. This may be characterized by a different relative buckling orientation. As can be seen in Table 1, the most stable configurations are “A”, “C” and “E” almost degenerate in energy; the remaining configurations, obtained by changing the relative orientation of the unsaturated Si dimers in the substrate, have a higher formation energy.

The result that the most favorable adsorption geometry for acetylene on  $Si(100)$  involves C–C double bonding is an evidence of the high stability of the C–C dimers, even at high temperature. Indeed, the C–C bond of acetylene was never broken during molecular dynamics simulations (simulated annealing) [4,8]. This stability may represent a difficulty for SiC growth, that might be avoided by

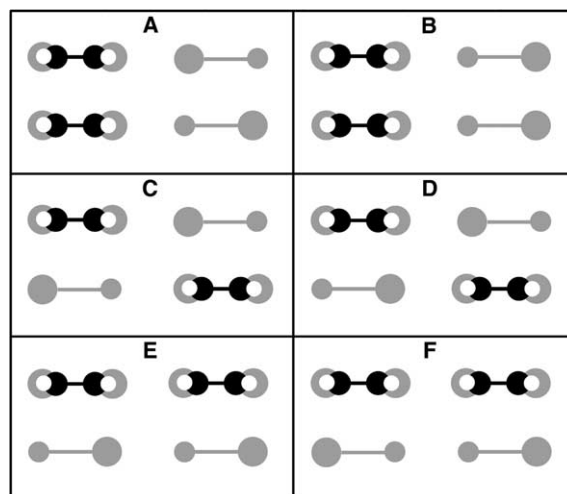


Fig. 2. Different possible structures of acetylene adsorbed on  $Si(100)$  in the “ $\gamma$ ” configuration, at 0.5 ML coverage. Gray balls represent surface dimers of Si atoms, black large balls and white smaller balls represent the adsorbed  $C_2H_2$  molecules. The Si dimers are buckled, smaller Si atoms (gray) are closer to the surface than the larger ones.

Table 1

Total energy per adsorbed molecule (relative to the “A” structure) for different structures of  $C_2H_2$  adsorbed on  $Si(100)$  in the “ $\gamma$ ” configuration (see Figs. 1 and 2), at 0.5 ML coverage

Configuration	Energy (meV)
A	0
B	89
C	2
D	18
E	3
F	17

heating the sample or by interaction with other molecules or atoms.

In Fig. 3, we present the optimized structures for the clean (left) and  $C_2H_2$ -covered (right)  $Si(111)\text{-}2\times 2$  surface. On the clean surface, the distance between the ad-atom and the rest-atom is in excellent agreement with that on the  $7\times 7$  reconstruction, indicating that our model is appropriate to attempt comparisons to experimental studies that suggest that  $C_2H_2$  molecules preferentially bridge rest-atom and ad-atom sites at the  $Si(111)\text{-}7\times 7$  surface. We find that, upon adsorption of one acetylene molecule bridging the

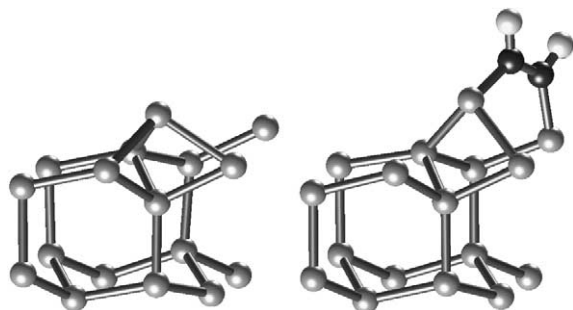


Fig. 3. Si(111)- $2\times 2$  model (left panel) of the ad-atom and rest-atom sites of the Si(111)- $7\times 7$ . The ad-atom to rest-atom distance is the same as in the  $7\times 7$  reconstruction. In the right panel the adsorption of  $C_2H_2$  in bridge configuration is presented. This stable geometry is characterized by double C–C bonding and breaking of a bond between the Si ad-atom and a Si surface atom.

ad-atom and the rest-atom, there is an energy gain of 1.85 eV per molecule. Also in this case, the C–C distance is 1.36 Å and the frequency of the C–C stretching mode is  $1457\text{ cm}^{-1}$  in good agreement with the previous result for adsorption on Si(001), and with experimental evidence [5].

The above considerations reveal that some features of  $C_2H_2$  adsorption on silicon are independent of the substrate orientation: on both the (100) and the (111) surfaces, in the high density regime represented by the chosen structures, the molecular C–C double bonds are not broken. For the (111) face, we also investigated different geometries with the molecule at the ad-atom site and lying parallel to the surface normal, as suggested by the HREELS data [5]. Preliminary results indicate that vertical geometries obtained by breaking one C–H bond and attaching the  $C_2H$  group to the rest-atom and the H atom to the ad-atom (and vice versa), are unfavorable. Therefore, at the present stage of our simulations, a full theoretical interpretation of the HREELS spectra is still lacking: in principle, the vertical adsorption may occur at another site of the  $7\times 7$  reconstruction which is not sampled in our surface model, for instance around a vacancy. The  $2\times 2$  model of the Si(111) surface allows us to investigate the adsorption of acetylene only around the ad-atom and the rest-atom. Despite there are clear experimental indications that this is the most interesting loca-

tion for a possible dissociation reaction of the molecule at the Si(111) surface, many adsorption configurations can be investigated to attain a complete picture of the energetics. Currently, we are examining the feasibility of more extended simulations that take into account vacancies and stacking faults of the  $7\times 7$  reconstruction. The analysis presented here should be intended as the microscopic study of a metastable state, which most likely needs to be complemented by the understanding of other metastable states.

The high stability of C–C dimers is a hindering factor for the growth of SiC by the acetylene precursor. However, Dufour and coworkers reported the evidence of low temperature SiC formation [2] with the carbidization of Si surfaces through acetylene molecules. To explain the SiC formation, a mechanism of C–C bond breaking must be found: We suggest that the interaction of the C–C dimer with free Si atoms dissociated from the Si substrate should play a relevant role to this purpose. Such an issue was out of the aim of our present comparative analysis and probably beyond the reach of ab initio calculations, but might be addressed in forthcoming investigations by the aid of semi-empirical parametrizations of the interactions for molecular dynamics.

To avoid the problem related to C–C dimers, we considered the adsorption of methylsilane on the Si(100) surface. The ab initio results obtained for these calculations [9] reveal that the  $SiH_3CH_3$  molecule chemisorbs dissociatively on Si(100): if dissociation occurs by interaction with the Si surface, the most likely process implies breaking of a Si–H bond while leaving intact the Si–C bond, suitable for SiC growth; the corresponding process based on breaking of the Si–C bond is found to be energetically less favored. These results suggest that the surface does not play a role in breaking the IV–IV bonds of the adsorbed molecules. For what concerns the (111) surface, we have shown this behavior only in relation to C–C bonds, whereas for what concerns the (100) surface, we have shown this behavior both for C–C and S–C bonds. For the SiC formation using the acetylene precursor, the breaking of the C–C dimers has to be found in the interaction of the dimers with atoms, e.g. Si atoms that can be taken out of the

surface through the interaction of hydrogen atoms obtained by the breaking of C–H bonds, or supplying further Si atoms by high temperature exchange reactions.

As a final investigation on the adsorption of acetylene on Si(100), in order to clarify the controversial experimental situation about the favorable adsorption sites, we have undertaken a study of the optical properties of different structures. Since the orientation of acetylene is completely different (orthogonal) in the two degenerate configurations  $\gamma$  and  $\delta$ , we aim at finding some clear-cut features in the optical spectra that are connected to this anisotropy. Thus, the reflectance anisotropy spectroscopy (RAS) should be a useful technique. RAS involves the interaction of polarized electromagnetic radiation with the surface (and bulk) electronic dipole moments. With this technique, the difference in reflectivity between two orthogonal polarization states of light falling at normal incidence on the sample surface is measured. When applied to the surface of an isotropic bulk crystal, there is no net contribution from the bulk. Under these conditions, the RAS signal arises from the surface. Within the repeated slab approach, the RAS is calculated after the method by Manghi et al. [10]. In principle, the correct procedure should be the calculation of the electronic states in a many body approach, including self-energy effects, and taking into account the electron-hole interaction and local-field effects to obtain the dielectric function. Actually, the determination of the single particle electron states using the DFT scheme offers generally a quantitative good picture and is still the state of the art when the many-body calculation is too cumbersome like in this case. The preliminary results obtained for configuration  $\gamma$  show that around 1.5 eV there is a strong reduction of anisotropy when compared with the clean Si(100) surface RAS. This negative peak in the RAS of clean surface is due to optical transitions involving dimer states, and its sign shows that at low energy the transitions are favored for light polarized along the dimer rows, meaning a strong interaction of the dimers along the rows [11]. Its reduction in the C<sub>2</sub>H<sub>2</sub> covered surface can be understood with a reduction of the inter-dimer interaction due to the presence of the molecule.

#### 4. Conclusions

Our results reveal that the adsorption of acetylene on different Si surfaces is characterized by geometries allowing the formation of single bonds between the surface Si atoms and the C atoms of the molecule. The presence of C–C double bond is revealed by the value of the C–C distance and by the frequency of the stretching mode. The high stability of the C–C dimer, resulting by the double bond, may inhibit growth of SiC and may be opposed by heating the surface or by interaction of the dimer with other atoms or molecules.

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