

Ab-initio study of the adsorption of acetylene on Si(001) surface

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We present the results of a first principles study of the adsorption of acetylene on Si(001). Several adsorption sites are investigated, and the electronic structures and reflectance anisotropy spectra (RAS) are calculated for the energetically most favorable geometries. We find that the end-bridge adsorption sites, both at 0.5 ML and at 1ML C₂H₂ coverage do not give metallic surfaces, at odd with other calculations. First principles study of optical properties for different configurations of acetylene adsorbed on Si(001) show a strong change of the spectra, thus suggesting that RAS experiments may give a definitive answer on the adsorption sites and saturation coverage.

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1 Introduction The adsorption of simple hydrocarbon molecules on Silicon surfaces is very important in the study of the growth of SiC, a strategic semiconductor material. Acetylene, in particular, thanks to its triple bond is a very reactive molecule and hence represents a promising carbon source for the heterogrowth of silicon carbide on silicon. For this reason it has been extensively studied both theoretically and experimentally. Even if acetylene is a simple molecule, still many aspects of its adsorption on Si(001) surface are not clarified, and results are often contradictory.

Many experimental techniques have been used to investigate the adsorption of C₂H₂ on Si, ranging from STM, to LEED, HREED, Auger, photoemission, and photoelectron diffraction [1–10], with results often leading to different conclusions. What seems to be clarified is the fact that at room temperature, and below, the adsorption of acetylene is not dissociative, and that upon annealing at 879 K the C–H bonds break and the hydrogen leaves the surface.

The saturation coverage is still under debate, ranging from 0.5 ML [4] (corresponding to one hydrocarbon molecule each second Silicon dimer) to 0.83 ML [3], interpreted as an effective 1ML coverage when Si defect-free surfaces are considered. Still, even the adsorption site of acetylene is under debate, and what happens to the surface silicon dimers upon C₂H₂ adsorption is controversial.

Theoretical studies are also numerous [10–17] and two main classes of possible adsorption geometries, the di-sigma and the tetra-sigma, have been discussed because they are compatible with experimental findings. The di-sigma class contains the adsorption sites where one hydrocarbon molecule bonds with two silicon atoms; the tetra-sigma class where one hydrocarbon molecule bonds to four silicon atoms. The tetra-sigma class is higher in energy: theoretical results have, in fact, shown that

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this configuration is thermodynamically unfavorable, so we concentrate our analysis on the di-sigma class. Within this class, two are the adsorption sites mainly under debate: the ‘on-top’ site, where acetylene adsorbs on top of a silicon dimer (Fig. 1a), and the ‘end bridge’ site, where the acetylene bridges two Si dimers within the same row (Fig. 1b). These two configurations for a coverage of 0.5 ML have been discussed as the most favorable ones, but recently Miotto and coworkers [16] have stated that the end-bridge structure gives a metallic surface and hence would be Peierls unstable.

For higher coverage, namely 1 ML coverage, it has been agreed that the most stable geometry is the 1ML end-bridge structure, with two acetylene molecules per 2×2 cell bridging two silicon dimers within the same row (Fig. 1d). However, also this structure has been recently discarded by Miotto et al. because of its metal character. In this paper, we present our first-principles calculation in order to shed some light on the still controversial problem of the adsorption site and saturation coverage of Si(001):C₂H₂.

2 Scheme of the calculations We have performed ab-initio Density Functional Theory calculations on Si(001) clean and upon C₂H₂ adsorption. The exchange correlation Functional has been evaluated within the Local Density Approximation and also within the Generalized Gradient Approximation (GGA, PW91 [18]). A repeated Silicon slab consisting of 12 atomic layers in a 2×2 geometry has been used, with the bottom surface saturated with hydrogen. A set of 8 k-points in the Irreducible part of the Brillouin Zone (IBZ) and an energy cutoff of 40 Ry was used for the geometry optimizations and for the calculations of the adsorption energy. This has been evaluated as:

$$E_{ads} = E[\text{Si} : \text{C}_2\text{H}_2] - E[\text{Si}(001) 2 \times 2] - E[\text{C}_2\text{H}_2] \quad (1)$$

where E is the energy of the Silicon surface covered with C₂H₂, of the clean Silicon surface, and of the isolated C₂H₂ molecule, respectively.

Optical properties have been computed using a set of 28 k-points in the IBZ. The Reflectance Anisotropy has been calculated following Del Sole [19] as:

$$\frac{R_x(\omega) - R_y(\omega)}{R_0(\omega)} = \frac{4\omega d}{c} \text{Im} \frac{4\pi(\alpha_{xx}^{hs}(\omega) - \alpha_{yy}^{hs}(\omega))}{\epsilon_b(\omega) - 1}, \quad (2)$$

with ϵ_b bulk dielectric function and α equal to the half slab polarizability. c is the light speed and d the half slab thickness. Here we have taken x as the direction of the dimers of the clean Si(001) surface.

3 Results The geometries studied, ranging from 0.5 ML (one acetylene molecule per 2×2 silicon cell) to 1 ML coverage (2 acetylene molecules per 2×2 cell) are shown in Fig. 3. In the on top geometry (Fig. 1a) the Silicon dimer bonded to the C₂H₂ is not buckled, whereas the Si dimer not bonded with acetylene preserves its buckling as in the clean Si(001) surface.

Interestingly, we have found two possible equilibrium bridge configurations for 0.5 ML, one almost symmetric (Fig. 1b), the other more stable and asymmetric (Fig. 1c). The asymmetry, not visible in

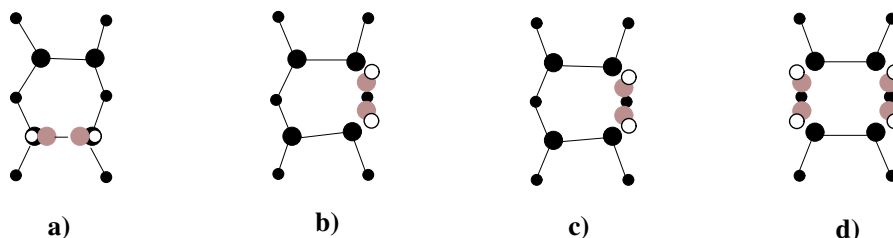


Fig. 1 (online colour at: www.interscience.wiley.com) Top view of the geometries studied: a) ‘on-top’, b) end-bridge symmetric 0.5 ML, c) end-bridge asymmetric 0.5 ML, d) end-bridge 1 ML coverage. Black circles: Si atoms; Gray circles: C atoms; white circles: H atoms.

Table 1 Adsorption energy per molecule, E_{ads} , and structural parameters for acetylene on Si(001). Si-Si(1) and Si-Si(2) indicate the Si dimers to which the acetylene molecule is bonded in the end-bridges configurations; in the case of the on-top structure the molecule is bonded only to the Si-Si(1) dimer. The buckling angles relative to these Si dimers are also given. Data have been computed using the gradient-corrected PW91 functional.

	on-top	end-bridge 0.5 ML asym.	end-bridge 0.5 ML symm.	1 ML end-bridge
E_{ads} (eV/C ₂ H ₂)	-2.75	-2.62	-2.54	-2.87
Si-Si(1) (Å)	2.33	2.42	2.39	2.41
buckling(1) (deg)	0.5	5.2	2.5	0.0
Si-Si(2) (Å)	2.29	2.38	2.39	2.41
buckling(2) (deg)	17.4	10.0	2.5	0.3
Si-C (Å)	1.88	1.90	1.90	1.90
C-C (Å)	1.34	1.35	1.35	1.35
C-H (Å)	1.09	1.09	1.09	1.09

the top view, is caused by the fact that the dimers are asymmetrically buckled in c), and symmetrically buckled in the b) geometry.

For 1 ML coverage (that is, 2 molecules of C₂H₂ on a Si(001) 2 × 2 cell), our calculated geometry shows that in the 1 ML end-bridge configuration the dimers are not buckled.

The geometrical details are listed in Tab. 1. In all cases considered, the silicon dimers do not break upon C₂H₂ adsorption.

3.1 Adsorption energies and electronic band structures The adsorption energies per C₂H₂ molecule, calculated according to Eq. 1, are shown in Tab. 1: for 0.5 ML coverage, the most stable structure is the on top one with an adsorption energy of -2.75 eV/C₂H₂. The corresponding band structure is shown in Fig. 2a. The asymmetric end-bridge is just 0.13 eV higher in energy and, at odd with the result of Miotto et al., turns out to be semiconducting (see Fig. 2b), though the minimum gap is only 0.35 eV. The two surface states within the gap are related to the ‘uppermost’ and ‘the most down’ Si surface atoms. The symmetric end-bridge geometry is higher in energy than the asymmetric one. Moreover, this structure turns out to be metallic. Our results hence show that the surface undergoes a spontaneous structural distortion from the symmetric end-bridge to the asymmetric end-bridge, lowering its energy by about 0.08 eV and becoming semiconducting.

Finally, for 1ML coverage, the end-bridge geometry is without doubt semiconducting (see Fig. 3): the Silicon dimers are not buckled anymore, the empty (full) surface states typical of the Si(001)

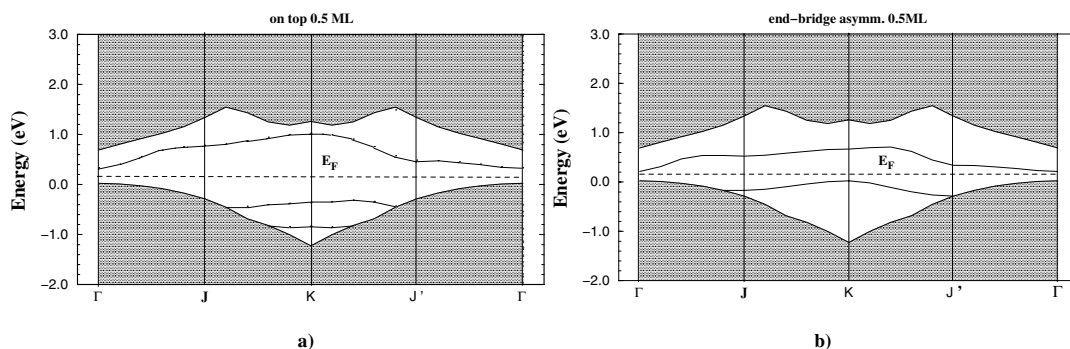


Fig. 2 a) Band structure for the on top band structure. Analysis of the surface states reveals that the filled (empty) surface state in the gap is related to the up (down) silicon atom belonging to the Si dimer not bonded to acetylene. b) Band structure for the end-bridge asymmetric structure 0.5 ML coverage. See text for details.

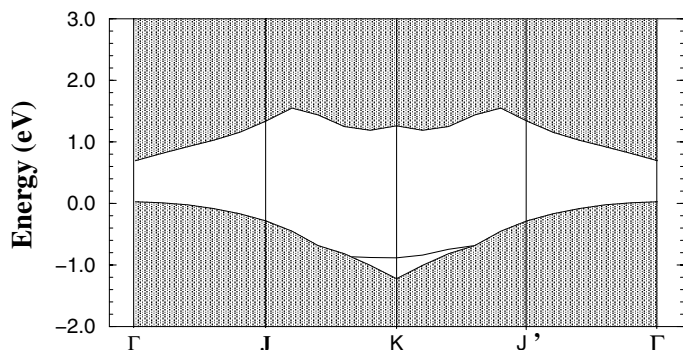


Fig. 3 Band structure for the end-bridge geometry at 1 ML coverage.

surface, connected to the ‘down’ (up) silicon atoms of the clean surface, are saturated, and the gap becomes empty (Fig. 3).

3.2 Optical properties Figure 4 shows our calculated Reflectance Anisotropy Spectra (RAS) obtained for the clean Si(001) surface and upon C_2H_2 adsorption. As it can be seen, at low photon energy (around 1.0 eV) there is a strong reduction of anisotropy for the on-top configuration with respect to the clean Si(001) surface, while in the end-bridge 0.5 ML configuration there is an opposite behavior with an increase of the negative peak. This negative peak in the RAS of the clean surface [20] (experimentally [21] a peak is found at 1.6 eV, the shift between theory and experiment being due to the well known underestimation of the energy gaps by DFT) is due to optical transitions involving silicon dimer states, and its sign shows that, at low energy, the transitions are favored for light polarized along the dimer rows, thus implying a strong interaction among the dimers along the same row. Therefore, the fact that this peak is reduced in the on-top configuration can be understood as a reduction of the interaction among the dimers, due to the presence of the chemisorbed acetylene molecule; instead, in the end-bridge configuration (at 0.5 ML coverage), since the axis of the molecule is perpendicular to the Si dimers, there is an increase of transitions for light polarized along this direction. Finally, for 1ML coverage, the anisotropy disappears because the acetylene saturates all the surface silicon bonds and the corresponding states are pushed out of the electronic gap.

Our RAS calculations suggest that a direct way to investigate the adsorption sites of C_2H_2 on Si(001) would be to perform reflectance anisotropy experiments in the near infrared regions. At these

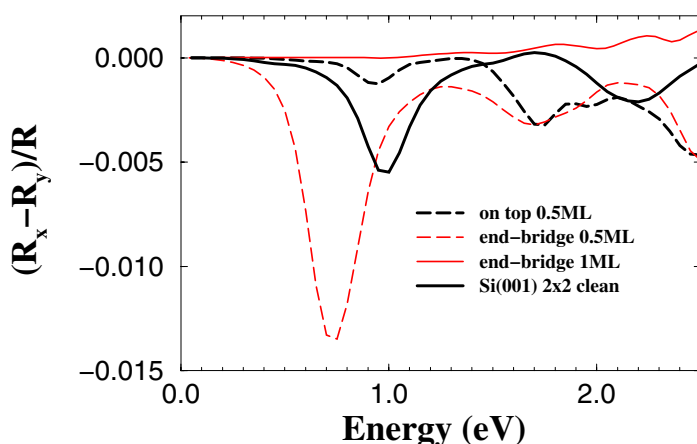


Fig. 4 (online colour at: www.interscience.wiley.com) Theoretical RAS for Si(001) 2×2 clean (thick solid line), on top (thick dashed line), end-bridge asymmetric 0.5ML (gray dashed line) and end-bridge at 1ML coverage (gray solid line).

energies a dramatic change in the spectra with respect to the clean Si(001) surface is predicted, due to the changes in the electronic structure within the silicon surface gap.

4. Summary and Conclusion We have presented an ab-initio calculation of the geometry, electronic structure and optical properties of acetylene on Si(001) surfaces. We found that the on-top geometry is, for 0.5 ML coverage, the most stable one, but the end-bridge is just 0.13 eV/C₂H₂ higher in energy and not metallic, caused by a spontaneous distortion (asymmetric buckling) that lowers the energy with respect to the symmetric buckled configuration, and makes the surface semiconducting. Moreover, the adsorption energy is lowest for the end-bridge 1 ML, thus suggesting that the saturation coverage could be one full monolayer. This structure, discarded in the past because claimed to be metallic, is in our calculations semiconducting. Finally, the theoretical RAS shows characteristic changes upon acetylene adsorption, indicating that experimental reflectance anisotropy spectra would help in discriminating the adsorption sites and saturation coverage.

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