

First-principles study of the adsorption of C_2H_2 and C_2H_4 on Si(100)

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The adsorption of acetylene and ethylene on the Si(100) surface is studied by first-principles density-functional calculations within the generalized gradient approximation. Both molecules are found to adsorb identically on the top of Si dimers, forming two σ bonds between C and Si atoms. This result does not support a recent photoelectron imaging observation where the adsorption sites of the two molecules differ from each other. Controversial issues, such as the intactness of the Si dimer bond and the saturation coverages of both adsorbed molecules, are discussed.

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The adsorption of acetylene and ethylene on the Si(100) surface has attracted much attention because of the technological importance of the formation of silicon carbide films as well as for fundamental aspects of the interaction of unsaturated hydrocarbon molecules with the dangling-bond states of semiconductor surfaces.^{1,2} Despite a wealth of experimental³⁻⁸ and theoretical⁹⁻¹¹ studies on both adsorbed molecules, several basic issues on the adsorption site, bonding characteristics, and saturation coverage are still controversial.

For the adsorption site of C_2H_2 and C_2H_4 on Si(100), various experimental studies using high-resolution electron-energy-loss spectroscopy,³ scanning tunneling microscopy (STM),⁴ near-edge x-ray-absorption fine structure (NEXAFS),⁵ and photoelectron diffraction (PhD)⁶ found that both molecules are adsorbed on the top of Si dimers, where the C-C bond is parallel to the Si dimer bond, by forming two σ bonds between C and Si atoms [see Fig. 1(a)]. However, a recent photoelectron imaging experiment carried out by Xu *et al.*⁷ observed an adsorption site for C_2H_2 [termed the tetra- σ model, Fig. 2(a)], where the carbon atoms sit between two Si dimers in the same dimer row, bonded to four Si surface atoms. Thus, Xu *et al.* argued that adsorbed C_2H_2 has the same bonding character of sp^3 with a single C-C bond as the case of adsorbed C_2H_4 . There was also a debate about the atomic structures for adsorbed C_2H_2 and C_2H_4 , i.e., whether upon their adsorption the Si dimer bond remains intact [termed the dimerized model, Fig. 1(a)] or is cleaved^{12,13} [termed the dimer-cleaved model, Fig. 1(b)]. The saturation coverages of C_2H_2 and C_2H_4 on Si(100) are still controversial. STM studies^{4,8} observed the adsorption of the C_2H_2 and C_2H_4 molecules on alternate Si dimer sites, and therefore an overlayer with $p(2 \times 2)$ or $c(4 \times 2)$ order was locally formed, leading to the saturation coverage of $\theta=0.5$ ML. However, an ultraviolet photoemission spectroscopy study with the kinetic uptake method determined the saturation coverage to be $\theta=1$ ML.¹⁴⁻¹⁶

In this work we study the adsorption of both C_2H_2 and C_2H_4 molecules on Si(100) for coverages of $\theta=0.5$ and 1 ML, using the same first-principles calculation scheme.^{17,18} Here the equilibrium geometries and energetics of the three existing models, i.e., dimerized, dimer-cleaved, and tetra- σ models, are considered. For both adsorbed molecules the dimerized model is found to be more stable than the dimer-cleaved model as well as the tetra- σ model, showing that the carbon atoms of adsorbed C_2H_2 and C_2H_4 form sp^2 and sp^3 bonding, respectively. This result supports the majority of the experimental data³⁻⁸ except that of a recent photoelectron imaging experiment,⁷ where the tetra- σ model was proposed for adsorbed C_2H_2 . Moreover, C_2H_4 molecules favor adsorption on alternate Si dimers rather than on neighboring dimers along a dimer row, because of the repulsive hydrogen-hydrogen interaction between adsorbed C_2H_4 . In contrast, in adsorbed C_2H_2 such H-H repulsion is not dominant. Based on the calculated adsorption energies for $\theta=0.5$ and 1 ML, we will discuss the controversy on the saturation coverage

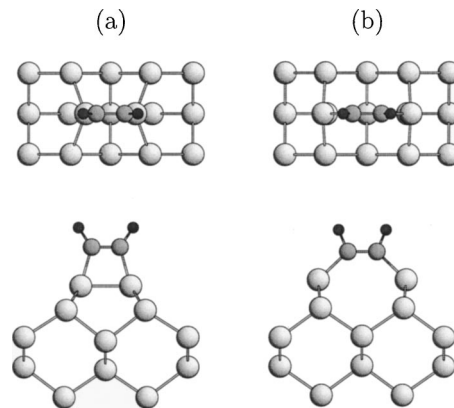


FIG. 1. Top and side views of the optimized geometry of adsorbed C_2H_2 on Si(100) with $\theta=1$ ML: (a) the dimerized model, and (b) the dimer-cleaved model. The large, medium, and small circles represent Si, C, and H atoms, respectively.

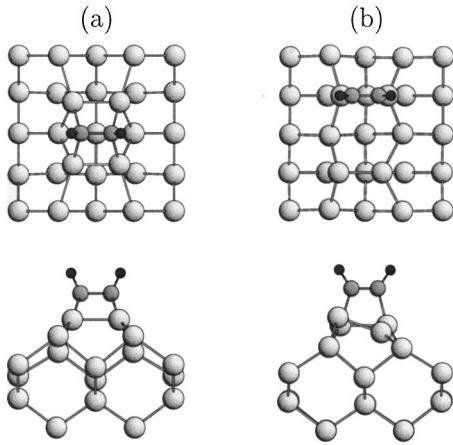


FIG. 2. Top and side views of the optimized geometry of adsorbed C_2H_2 on Si(100) with $\theta=0.5$ ML: (a) the tetra- σ model, and (b) the dimerized model.

for adsorbed C_2H_2 and C_2H_4 on Si(100).

Our first-principles calculations are performed using the plane-wave-basis pseudopotential method within the generalized gradient approximation (GGA).^{19,20} We use the exchange-correlation functional of Perdew, Burke, and Ernzerhof²⁰ for the GGA. The Si and H atoms are described by the norm-conserving pseudopotentials of Troullier and Martins,²¹ and the C atom is described by the ultrasoft pseudopotential of Vanderbilt.²² The Si surface is modeled by a periodic slab geometry consisting of 12 atomic layers and a vacuum region of seven such layers. The C_2H_2 and C_2H_4 molecules are adsorbed on both sides of the slab. The electron wave functions are expanded in a plane-wave basis set with a kinetic-energy cutoff of 25 Ry. The \mathbf{k} -space integration is done with eight and four points in the surface Brillouin zone of the 2×1 and 2×2 unit cells, respectively.²³ The positions of all atoms, except that the innermost two Si layers hold at their bulk positions, are allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components are less than 0.03 eV/Å.

First we determine the atomic structure of adsorbed C_2H_2 on Si(100)-(2×1) for the coverage of $\theta=1$ ML within the dimerized and dimer-cleaved models. The optimized structures for both models are shown in Fig. 1. The calculated adsorption energies (E_{ads}) and bond lengths are compared with previous theoretical data in Table I.²⁴ We find that the dimerized model [Fig. 1(a)] is more stable than the dimer-cleaved model [Fig. 1(b)] by $\Delta E_{\text{ads}}=1.07$ eV, in good agreement with a previous GGA calculation ($\Delta E_{\text{ads}}=1.04$ eV). Note that the local-density-approximation (LDA) calculation carried out by Fisher *et al.*¹¹ yielded a smaller adsorption energy (2.38 eV) than the GGA results (2.81 eV, obtained by Imamura *et al.*⁹ and 2.74 eV in the present calculation). This seems to be off the general trend that the LDA overestimates the adsorption energy in adsorbed molecule systems compared to the GGA.²⁵ However, all theoretical calculations give similar bond lengths, in reasonable agreement with the experimental data (see Table I).

In order to compare the energetics for adsorbed C_2H_2 between the dimerized model and the tetra- σ model, we optimize both atomic structures with a coverage of $\theta=0.5$ ML, based on the experimental coverage in the tetra- σ model.⁷ The optimized structures for both models are shown in Fig. 2. We find that the dimerized model [Fig. 2(b)] is energetically more stable than the tetra- σ model [Fig. 2(a)] by $\Delta E_{\text{ads}}=1.60$ eV (see Table I). Thus our total-energy calculations do not support the recent photoelectron imaging experimental observation of the tetra- σ structure,⁷ in which adsorbed C_2H_2 adopts an sp^3 carbon hybridization by leaving just a single bond between the carbon atoms. Moreover, the bond lengths and interplanar separations reported in Ref. 7 show a large discrepancy from our theory (see Table II). Note that the reported C-C bond length ($d_{\text{C-C}}$) of 1.1 Å is shorter than that of an isolated C_2H_2 molecule ($d_{\text{C-C}}\approx 1.2$ Å), and is much too short to be consistent with the sp^3 bonding character in the tetra- σ model. On the other hand, our value of $d_{\text{C-C}}$ (1.55 Å) in the tetra- σ model of adsorbed C_2H_2 is very close to that (1.56 Å) in the dimerized model of adsorbed C_2H_4 , which has sp^3 carbon hybridization.

TABLE I. Calculated adsorption energy (eV/molecule) and bond lengths (Å) for adsorbed C_2H_2 on Si(100), in comparison with previous theoretical and experimental results.

Model		coverage	E_{ads}	$d_{\text{C-C}}$	$d_{\text{C-Si}}$	$d_{\text{Si-Si}}$
dimerized	PW (GGA) ^a	1 ML	2.81	1.36	1.90	2.36
	PAW (LDA) ^b	0.25 ML	2.38	1.37		2.40
	This (GGA)	1 ML	2.74	1.37	1.91	2.37
	This (GGA)	0.5 ML	2.72	1.37	1.91	2.37
	NEXAFS ^c			1.36±0.04		
	PhD ^d			1.36±0.19	1.83±0.04	2.44±0.58
cleaved	PW (GGA) ^a	1 ML	1.77	1.37	1.93	4.13
	This (GGA)	1 ML	1.67	1.37	1.94	4.16
tetra- σ	This (GGA)	0.5 ML	1.12	1.55	2.06	2.37

^aReference 9.

^bReference 11.

^cReference 5.

^dReference 6.

TABLE II. Calculated bond lengths (\AA) and interlayer spacings (\AA) for adsorbed C_2H_2 on Si(100) within the tetra- σ model, in comparison with those in Ref. 7. Si(1) and Si(2) denote the first- and second-layer Si atoms, respectively.

	$d_{\text{C-C}}$	$d_{\text{C-Si}}$	$h_{\text{C-Si(1)}}$	$h_{\text{C-Si(2)}}$
This	1.55	2.06	1.30	2.90
Ref. 7	1.1	1.8	0.8	1.6

Similarly, we performed the geometry optimization for adsorbed C_2H_4 on Si(100) within the dimerized, dimer-cleaved, and tetra- σ models. The calculated adsorption energies and bond lengths are compared with those of previous calculations^{9–11} in Table III, together with the experimental data.^{5,6} For $\theta=1$ ML, the dimerized model [Fig. 3(a)] is found to be more stable than the dimer-cleaved model by $\Delta E_{\text{ads}}=1.14$ eV. This is comparable to the LDA result ($\Delta E_{\text{ads}}=1.11$ eV) obtained by Pan *et al.*¹⁰ Their LDA values for the adsorption energy are larger than our GGA ones, while the LDA calculations carried out by Fisher *et al.*¹¹ gave too small an adsorption energy, as mentioned above in adsorbed C_2H_2 (see Table III). It is interesting to note that in adsorbed C_2H_4 the tetra- σ model is unstable compared to the gas phase. As shown in Table III, the bond lengths of all theoretical calculations agree well with experiments.

Using core-level x-ray photoemission, Rochet *et al.*²⁶ found that the adsorption of C_2H_4 on Si(100) occurs easily, with a sticking coefficient of nearly unity up to a critical coverage $\theta_c=0.5$ ML, after which the adsorption rate decreases strongly, but the completion of 1 ML is allowed if the surface is exposed to large dose of ~ 2330 ($1 \text{ L} = 10^{-6}$ Torr s). This saturation coverage of 1 ML is consistent with the kinetic uptake measurements of Cheng *et al.*¹⁴ and Clemen *et al.*¹⁵ At low coverage the STM measurement of Mayne *et al.*⁸ found that the C_2H_4 molecules “prefer” to adsorb on alternate dimer sites, creating either a local $p(2\times 2)$ structure or a $c(4\times 2)$ structure. Based on the above experimental observations, it is expected that for θ

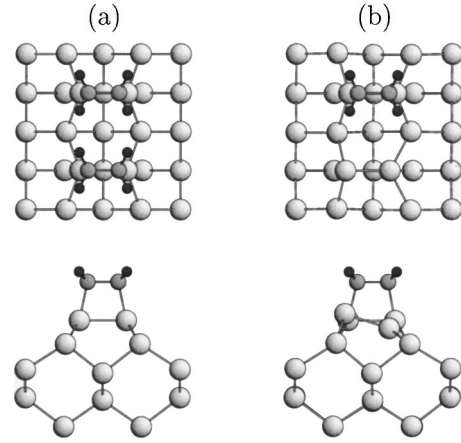


FIG. 3. Top and side views of the optimized geometry of adsorbed C_2H_4 on Si(100): (a) $\theta=1$ ML and (b) $\theta=0.5$ ML.

$< \theta_c$ the adsorption of C_2H_4 on neighboring Si dimers is avoided by some repulsive interaction between adsorbed molecules.⁸ In order to estimate this repulsive interaction, we consider a large unit cell of $p(2\times 2)$ in which the C_2H_4 molecules are well separated. The optimized atomic structure of $p(2\times 2)$ with $\theta=0.5$ ML is given in Fig. 3(b). We find that the adsorption energy for $\theta=0.5$ ML increases by 0.04 eV compared to that for $\theta=1$ ML (see Table III). The lower stability at $\theta=1$ ML is possibly due to the repulsive H-H interaction between the nearby C_2H_4 molecules: Note that the intermolecular H-H distance in Fig. 3(a) is short (2.10 \AA). Because the adsorption energy difference between $\theta=0.5$ and 1 ML is small ($\Delta E_{\text{ads}}=0.04$ eV), we believe that the large doses of C_2H_4 molecules may overcome the repulsive H-H interaction to saturate all dangling bonds of the Si dimers.

Unlike in adsorbed C_2H_4 , we find that in adsorbed C_2H_2 the adsorption energy for $\theta=1$ ML ($E_{\text{ads}}=2.74$ eV) is slightly larger than that for $\theta=0.5$ ML ($E_{\text{ads}}=2.72$ eV). This indicates that the H-H interaction between the nearby C_2H_2 molecules at $\theta=1$ ML does not prevent adsorption

TABLE III. Calculated adsorption energy (eV/molecule) and bond lengths (\AA) for adsorbed C_2H_4 on Si(100), in comparison with previous theoretical and experimental results.

Model		coverage	E_{ads}	$d_{\text{C-C}}$	$d_{\text{C-Si}}$	$d_{\text{Si-Si}}$
dimerized	PW (LDA) ^a	1 ML	2.63	1.52	1.93	2.33
	PAW (LDA) ^b	0.25 ML	1.57	1.53		2.39
	This (GGA)	1 ML	1.89	1.56	1.96	2.37
	This (GGA)	0.5 ML	1.93	1.56	1.95	2.37
	NEXAFS ^c			1.52 \pm 0.04		
	PhD ^d			1.62 \pm 0.08	1.90 \pm 0.01	2.36 \pm 0.21
cleaved	PW (LDA) ^a	1 ML	1.52	1.56	1.95	4.25
	This (GGA)	1 ML	0.75	1.60	1.97	4.24
tetra- σ	This (GGA)	0.5 ML	-0.56	1.35	3.85	2.40

^aReference 10.

^bReference 11.

^cReference 5.

^dReference 6.

on the neighboring Si dimer. Thus we anticipate that the kinetical aspects of C_2H_2 adsorption differ from the case of C_2H_4 adsorption. On the other hand, a STM study for adsorbed C_2H_2 observed either a local $p(2 \times 2)$ structure or a $c(2 \times 4)$ structure.⁴ Although this ordering in adsorbed C_2H_2 has not been explained by the present total-energy calculations, its origin may be explained by a dipole interaction between the gas-phase C_2H_2 and adsorbed C_2H_2 molecules via a mobile precursor mechanism,²⁷ as suggested by Li *et al.*⁴

In conclusion, our first-principles calculations showed that both C_2H_2 and C_2H_4 molecules adsorb identically on top of a Si dimer, forming two σ bonds between C and Si atoms.

This result supports the majority of the experimental data, except for a recent photoelectron imaging experiment. Moreover, we found that adsorbed C_2H_4 molecules on neighboring Si dimers have a repulsive H-H interaction, whereas in adsorbed C_2H_2 molecules such interaction disappears. Our calculated adsorption energies for coverages of 0.5 and 1 ML provide some information for the saturation coverages which is still controversial in experiments.

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- ¹J.T. Yates, Jr., *Science* **279**, 335 (1998).
²G.P. Lopinski, D.J. Moffatt, D.D.M. Wayner, and R.A. Wolkow, *Nature (London)* **392**, 909 (1998).
³M. Nishijima, J. Yoshinobu, H. Tsuda, and M. Onchi, *Surf. Sci.* **192**, 383 (1987).
⁴L. Li, C. Tindall, O. Takaoka, Y. Hasegawa, and T. Sakurai, *Phys. Rev. B* **56**, 4648 (1997).
⁵F. Matsui, H.W. Yeom, A. Imanishi, K. Isawa, I. Matsuda, and T. Ohta, *Surf. Sci.* **401**, L413 (1998).
⁶R. Terborg, P. Baumgärtel, R. Lindsay, O. Schaff, T. Giebel, J.T. Hoeft, M. Polcik, R.L. Toomes, S. Kulkarni, A.M. Bradshaw, and D.P. Woodruff, *Phys. Rev. B* **61**, 16 697 (2000).
⁷S.H. Xu, M. Keefe, Y. Yang, C. Chen, M. Yu, G.J. Lapeyre, E. Rotenberg, J. Denlinger, and J.T. Yates, Jr., *Phys. Rev. Lett.* **84**, 939 (2000).
⁸A.J. Mayne, A.R. Avery, J. Knall, T.S. Jones, G.A.D. Briggs, and W.H. Weinberg, *Surf. Sci.* **284**, 247 (1993).
⁹Y. Imamura, Y. Morikawa, T. Yamasaki, and H. Nakatsuji, *Surf. Sci.* **341**, L1091 (1995).
¹⁰W. Pan, T. Zhu, and W. Yang, *J. Chem. Phys.* **107**, 3981 (1997).
¹¹A.J. Fisher, P.E. Blöchl, and G.A.D. Briggs, *Surf. Sci.* **374**, 298 (1997).
¹²C. Huang, W. Widdra, X.S. Wang, and W.H. Weinberg, *J. Vac. Sci. Technol. A* **11**, 2250 (1993); C. Huang, W. Widdra, and W.H. Weinberg, *Surf. Sci.* **315**, L953 (1994).
¹³W. Widdra, C. Huang, G.A.D. Briggs, and W.H. Weinberg, *J. Electron Spectrosc. Relat. Phenom.* **64/65**, 129 (1993).
¹⁴C.C. Cheng, R.M. Wallace, P.A. Taylor, W.J. Choyke, and J.T. Yates, Jr., *J. Appl. Phys.* **67**, 3693 (1990).
¹⁵L. Clemen, R.M. Wallace, P.A. Taylor, W.J. Choyke, M.J. Dresser, W.H. Weinberg, and J.T. Yates, Jr., *Surf. Sci.* **268**, 205 (1992).
¹⁶C.C. Cheng, P.A. Taylor, R.M. Wallace, H. Gutleben, L. Clemen, M.L. Colainanni, P.J. Chen, W.H. Weinberg, W.J. Choyke, and J.T. Yates, Jr., *Thin Solid Films* **225**, 196 (1993).
¹⁷J.-H. Cho, K.S. Kim, S.H. Lee, and M.H. Kang, *Phys. Rev. B* **61**, 4503 (2000).
¹⁸J.-H. Cho and K.S. Kim, *Phys. Rev. B* **62**, 1607 (2000).
¹⁹P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965).
²⁰J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996); **78**, 1396(E) (1997).
²¹N. Troullier and J.L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
²²D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *ibid.* **47**, 10 142 (1993).
²³A higher level calculation [$E_{pw}=30$ Ry and $N_k=32$ in the 2×1 unit cell] hardly changes the bond lengths and relative stabilities (within 0.01 eV). Our calculation scheme was successfully applied for the adsorption of H_2O (Ref. 17) and NH_3 (Ref. 18) on Si(100).
²⁴For the calculation of the adsorption energy, the total energy of the clean Si(100) surface is referred to the $p(2 \times 2)$ reconstructed surface and those of the isolated C_2H_2 and C_2H_4 molecules are obtained using $10 \times 10 \times 15$ -Å³ supercell calculation.
²⁵M. Sprik, J. Hutter, and M. Parrinello, *J. Chem. Phys.* **105**, 1142 (1996), and references therein.
²⁶F. Rochet, F. Jolly, F. Bournel, G. Dufour, F. Sirotti, and J.-L. Cantin, *Phys. Rev. B* **58**, 11 029 (1998).
²⁷P.A. Taylor, R.M. Wallace, C.C. Cheng, W.H. Weinberg, M.J. Dresser, W.J. Choyke, and J.T. Yates, Jr., *J. Am. Chem. Soc.* **114**, 6754 (1992).