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First-principles molecular dynamics study of acetylene adsorption on the Si(001) surface

Y. Imamura^a, Y. Morikawa^{a,b,1}, T. Yamasaki^{b,c}, H. Nakatsuji^{a,d,*}^a Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan^b Joint Research Center for Atom Technology (JRCAT), 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan^c Angstrom Technology Partnership (ATP), 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan^d Institute for Fundamental Chemistry, Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan

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Abstract

We present a first-principles molecular dynamics study of acetylene adsorption on the Si(001) surface. Acetylene molecules are di- σ bonded to the first layer Si dimers with the adsorption energy of 64.8 kcal/mol. It is elucidated that the CC bond is essentially double bond and the Si dimer bonds are not cleaved. The normal mode analyses well reproduce the experimental results, giving a strong support to our results.

Keywords: Alkynes; Chemisorption; Density functional calculations; Silicon; Vibrations of adsorbed molecules

The interaction of organic molecules with well-defined Si surfaces is an interesting subject because it is important to understand the elementary steps of chemical vapor deposition (CVD) of silicon carbide, which is a promising semiconductor material [1,2]. C₂H₂ adsorption on the Si(001) surface has been studied by using various surface science techniques as well as empirical and semi-empirical theoretical methods [3–9], however, the fundamental aspects of the adsorption state are controversial.

Nishijima et al. [3] employed low energy

electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS) to study the adsorption and thermal decomposition of C₂H₂ on the Si(001) surface. They assigned an energy loss peak at 1090 cm⁻¹ to the CC stretching mode and concluded that C₂H₂ is di- σ bonded to the dangling bonds of the first layer Si dimer with the C–C rehybridization state of sp³ (see Fig. 1a). On the other hand, Taylor and co-workers [5] argued that the adsorbed C₂H₂ should have the sp² rehybridization state rather than sp³ and the substrate Si dimer should be cleaved to make an appropriate bond angle between the C=C bond and the Si–C bond (Fig. 1b). Huang et al. [7] performed HREELS experiment and found a new peak at 1450 cm⁻¹, which had not been observed by Nishijima's group, and assigned it to the CC

*Corresponding author. Fax: +81 75 753 5910.

¹Present address: Joint Research Center for Atom Technology (JRCAT), National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan.

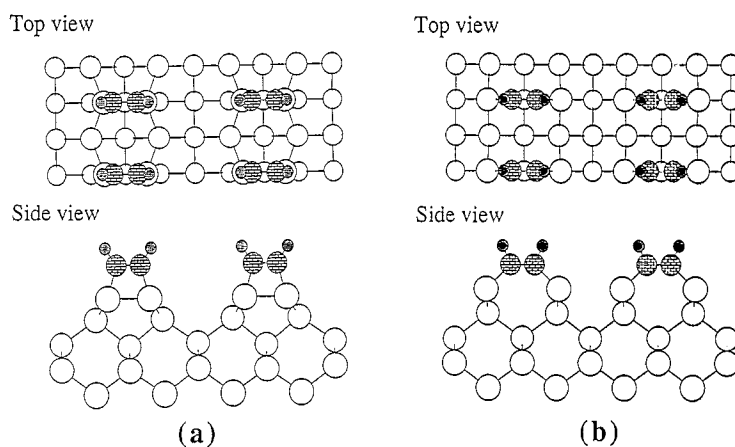


Fig. 1. Top views and side views of structure models of the $C_2H_2/Si(001)$ surface. (a) The dimerized model, and (b) the dimer-cleaved model. Open circles, hatched circles, and solid circles indicate Si, C, and H atoms, respectively.

stretching mode, being consistent with the latter model. Several empirical and semi-empirical theoretical studies have been done for the system [4,6,8,9]. Among them, the substrate structural relaxations were taken into account only by Craig and Smith [6] and Carmer et al. [9]. Both studies prefer the dimer-cleaved model with dimer bond length of 3.47 Å [9] and 3.66 Å [6], which are much larger than the bulk Si–Si bond length of 2.35 Å. In the present study, we have performed first-principles molecular dynamics [10] calculations of the $C_2H_2/Si(001)$ surface to clarify the stable structure and electronic properties of the surface.

Our calculation is based on the generalized gradient approximation (GGA) in density functional theory (DFT) and Perdew and Wang's formula is used for the exchange-correlation energy and potential [11–15]. The GGA exchange-correlation potential is calculated by using a method of White and Bird [16]. We have constructed the pseudopotential following Troullier and Martins' optimized norm-conserving pseudopotential scheme [17,18] except for the carbon p state, for which we have used Vanderbilt's ultrasoft pseudopotential scheme [19]. We used a repeated slab geometry in which each slab consists of ten Si layers and the vacuum region with seven Si layers thickness. The lattice constant of the Si slabs used in our calculations is determined from self-consistent GGA calculations of bulk Si. The C_2H_2 mole-

cules are adsorbed on both surfaces of a slab and all atomic positions except for the two center Si layers are relaxed. The cutoff energies for wave function and charge density expansion are 25 and 169 Ry, respectively. Two inequivalent k -points in a $1/4$ surface Brillouin zone are used for Brillouin zone sampling.

We have performed geometry optimization for the dimerized and dimer-cleaved models of the $C_2H_2/Si(001)$ surface and found that both structures are stable or metastable. In Fig. 2, the optimized structures for (a) the dimerized and (b) the dimer-cleaved models are shown and the structural parameters and the adsorption energies are indicated in Table 1. Our calculation shows that the dimerized structure is more stable than the dimer-cleaved structure by 24 kcal/mol and seems to support the Nishijima model [3], though, the obtained structure does not correspond to their original structural model. We found that in both models, the H, C and first layer Si atoms lie on the same plane and the CC bond distance is close to that of ethylene (1.34 Å) suggesting the sp^2 rehybridization state of the CC bond. The CCSi angles are very different in the two models: 105° for the dimerized structure while 136° for the dimer-cleaved structure. In the dimerized structure, the Si dimer bond length of 2.36 Å is only slightly longer than that of 2.31 Å in the clean Si(001) surface, while that of 4.13 Å in the dimer-cleaved structure is much larger and even larger than that

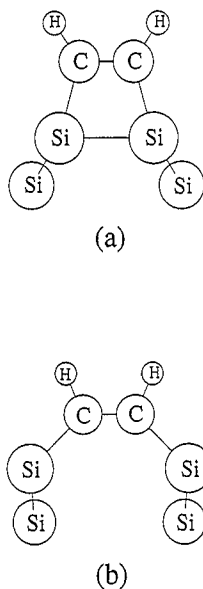


Fig. 2. Optimized structures of the $C_2H_2/Si(001)$ surface for (a) the dimerized structure and (b) the dimer-cleaved structure.

Table 1

Calculated structural parameters (Å) and the adsorption energy (kcal/mol) of C_2H_2 adsorbed on the Si(001) surface

	Dimerized model	Cleaved model	Free system
$R(Si-Si)$	2.36	4.13	2.31
$R(C-C)$	1.36	1.37	1.21
$R(Si-C)$	1.90	1.93	
Adsorption energy	64.8	40.8	

of the unreconstructed 1×1 surface. The experimentally determined zero coverage limit of the activation energy for desorption is 46.1 kcal/mol, which is much smaller than the theoretical adsorption energy of 64.8 kcal/mol for the dimerized structure [5]. The error of GGA in the atomization energy of C_2H_2 is reported to be less than 3% (9.2 kcal/mol) [14] and that in the cohesive energy of bulk Si to be less than 1% (0.23 kcal/mol) [15]. Therefore, the discrepancy between the adsorption energy and the desorption barrier is too large to be attributed to the error of GGA calculation. Because the desorption temperature is rather high (above 700 K), we suspect that the desorption occurs through some intermediate states.

To understand the electronic structure of these surfaces, we have calculated the partial electron charge density which is defined by

$$\rho^p(\mathbf{r}) = \sum_{i,k}^{\epsilon_{HOMO}-1 \text{ eV} \leq \epsilon_{i,k} \leq \epsilon_{HOMO}} w_k \rho_{i,k}(\mathbf{r}), \quad (1)$$

where ϵ_{HOMO} is the highest occupied level of the system, i the band index, k the k -point vector in the Brillouin zone, w_k the weight of the k -point sampling, and $\rho_{i,k}(\mathbf{r})$ the charge density due to the state $\{i, k\}$. In Fig. 3, partial electron charge densities for (a) the dimerized structure and (c) the dimer-cleaved structure on the cut planes perpendicular to the surface are shown. In the dimerized structure, there is no indication of the dangling bond state whereas, in the dimer-cleaved structure, there are two lobes extending between the two adjacent first-layer Si atoms originated from the dangling bond states. It is also important to note that in the dimerized structure, the partial charge density increases at the first layer Si dimer bond compared to other Si–Si bonds, indicating a weakening of the dimer bond due to the C_2H_2 adsorp-

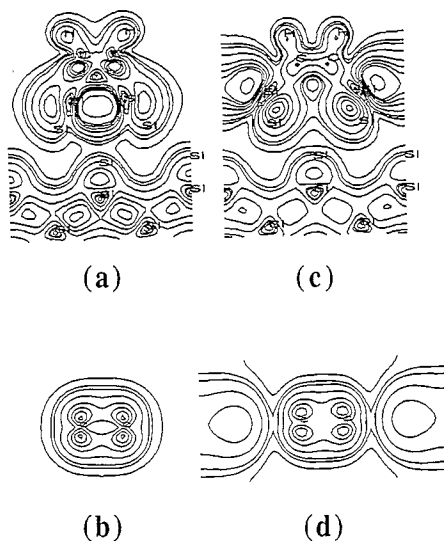


Fig. 3. The partial electron charge densities of the $C_2H_2/Si(001)$ surface for (a) and (b) the dimerized model and for (c) and (d) the dimer-cleaved model. The cut planes of (a) and (c) are perpendicular to the surface and contain the H, C and first layer Si atoms. The cut planes of (b) and (d) are parallel to the surface and contain the C atoms. Contours correspond to charge densities of 0.0003, 0.0007, 0.001, 0.002, 0.004, 0.006, 0.008, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1.

tion. This point may be important in the C_2H_2 decomposition and β -SiC formation process. The partial electron charge densities on the cut planes parallel to the surface for the dimerized and the dimer-cleaved structures are shown in Figs. 3b and 3d, respectively. In both structures, π -bond charge densities are clearly seen and indicate sp^2 rehybridization.

We have calculated the energy barrier for the change from the dimerized structure to the dimer-cleaved structure and the result is shown in Fig. 4. The constraint is imposed on the Si-Si dimer bond length, but other degrees of freedom are fully optimized. The energy barrier for the dimer cleavage on the $C_2H_2/Si(001)$ surface is 26 kcal/mol, which is much smaller than the adsorption energy of 64.8 kcal/mol. Although the dimerized structure is more stable than the dimer-cleaved structure, we think that the latter structure may be taken instantaneously just after the adsorption and the Si-Si bond-breaking and rebonding oscillation occurs until the adsorption energy is dissipated as discussed in Ref. [9] (in their calculation, however, the dimer-cleaved structure was calculated to be more stable than the dimerized structure).

We have performed the vibrational normal mode analyses of the dimerized structure and the dimer-

cleaved structure to get further information about the bonding. The normal vibrational modes are calculated by diagonalizing the matrix of the mass-weighted Cartesian force constant, which was obtained by the numerical finite difference method. To estimate the error in our vibrational mode analyses, we have calculated the vibrational modes of free C_2H_2 and H_2 molecules and compared with the experimental results. The error in the H-H stretching mode is large (-11%), but, the largest error in the normal modes of C_2H_2 is less than 4.0%. In Table 2, the calculated vibrational modes along with the experimental results are indicated. For the C-H stretching mode, the C-Si symmetric stretching mode, and the C-H out-of-plane symmetric stretching mode, the dimerized structure gives much closer results to the experimental values than the dimer-cleaved structure. Only the C-H in-plane asymmetric bending mode of the dimerized structure is worse than that of the dimer-cleaved structure. As for the CC stretching mode, for which two experiments gave different assignment, the two structures give almost the same frequencies: 1479 cm^{-1} for the dimerized structure and 1462 cm^{-1} for the dimer-cleaved structure which are in good agreement with Huang et al.'s assignment, indicating the sp^2 hybridization of the CC bond. Nishijima et al. [3] tentatively assigned 820 cm^{-1} to the asymmetric Si-C mode, but our simulation shows that this mode should be much softer.

In summary, we have performed first-principles molecular dynamics calculation of the acetylene-adsorbed Si(001) surface. The dimer-cleaved structure proposed by Taylor et al. was preferred by the previous empirical and semi-empirical calculations; however, the dimerized structure which was originally proposed by Nishijima et al. [3] is found to be more stable in the present study. Although the CCSi angle in the dimerized structure is much smaller than 120° , the CC bond has sp^2 character which is the key for the stability of the structure. The vibrational mode analyses give fairly good agreement with experiment, which gives a strong confirmation of the present result.

After completion of the present work, we found that Liu and Hoffmann [J. Am. Chem. Soc. 117

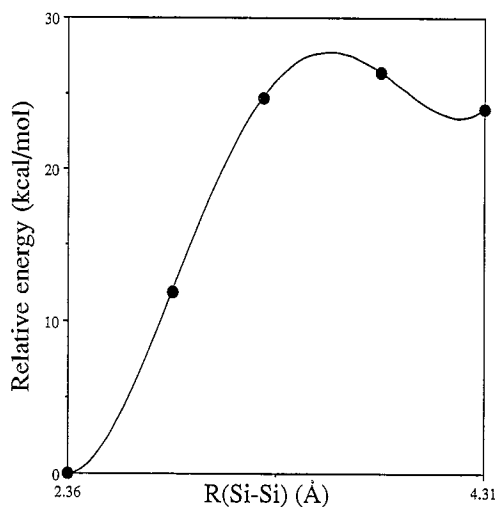


Fig. 4. The energy diagram of the reaction from the dimerized structure to the dimer-cleaved structure. The constraint is imposed on the Si-Si dimer bond length and other ionic degrees of freedom are fully optimized.

Table 2

Calculated and experimental vibrational frequencies (cm^{-1}) of $\text{C}_2\text{H}_2(\text{C}_2\text{D}_2)$ adsorbed on the Si(001) surface

Mode	EELS ^a	EELS ^b	Dimerized model	Cleaved model
C–H stretching	3000	2980	2990, 3011	2939, 2915
C–C stretching	1090	1450	1479	1462
C–Si stretching (asym.)	(820)		688	627
C–Si stretching (sym.)	690	680	693	530
C–H bending (in-plane, asym.)	1255	1240	1193	1253
C–H bending (in-plane, sym.)	(1090)		1002	1150
C–H bending (out-of-plane asym.)	970	1065	939	948
C–H bending (out-of-plane sym.)		680	671	590
C–D stretching	2250	2225	2220, 2210	2165, 2134
C–C stretching	1040	1420	1446	1447
C–Si stretching (asym.)			605	578
C–Si stretching (sym.)	675	670	673	524
C–D bending (in-plane, asym.)	890	1030	995	991
C–D bending (in-plane, sym.)	780		722	815
C–D bending (out-of-plane asym.)		780	745	739
C–D bending (out-of-plane sym.)	540	530	539	516

^a Ref. [3] ^b Ref. [7]

(1995) 4082] studied the same system by using the density functional theory (DFT) with the local density approximation (LDA), Hartree-Fock, and the extended Hückel methods, and suggested that the dimerized model is more stable, though, they do not relax the Si substrate.

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