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Structure and binding energies of unsaturated hydrocarbons on Si(001) and Ge(001)

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The adsorption of acetylene, ethylene, and benzene on the Si(001) and Ge(001) surfaces is investigated by first-principles density-functional calculations within the generalized-gradient approximation. We find that the adsorption energies of the three hydrocarbons containing a triple bond, a double bond, and a π-conjugated aromatic ring decrease as the sequence of $C_2H_2 > C_2H_4 > C_6H_6$. We also find that the bondings of acetylene, ethylene, and benzene to Ge(001) are much weaker than those to Si(001). As a result, benzene is weakly bound to Ge(001) while it is chemisorbed on Si(001), consistent with temperature-programed desorption data. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2151176]

The adsorption of unsaturated hydrocarbon molecules on the Si(001) and Ge(001) surfaces is of considerable interest because of its potential in technological applications such as nonlinear optical devices, chemical sensors, and molecular electronic devices.[1,2] The two surfaces exhibit the same surface reconstruction consisting of rows of buckled dimers in which two surface atoms bond to each other with a strong σ bond and a weak π bond. Therefore, the adsorption structures of unsaturated hydrocarbons on Si(001) and Ge(001) are expected to be similar to each other. A number of previous works[3–20] established that unsaturated hydrocarbons containing a $C \equiv C$ triple bond, a $C = C$ double bond, or a π-conjugated aromatic ring (e.g., acetylene,[3–10] ethylene,[11–16] and benzene[17–20]) are attached to the (001) surface of Si (Ge) through the so-called [2+2] cycloaddition reaction, where the π bond of unsaturated hydrocarbons interacts with the π bond of the Si (Ge) dimer, forming a four-membered ring with two new Si—C (Ge—C) σ bonds (see Fig. 1). Recent scanning tunneling microscopy experiments for adsorbed acetylene[6,7] and benzene[18–20] on Si(001) observed multiple adsorption structures, whereas several experiments[11–16] seem to agree that adsorbed ethylene on Si(001) has a single adsorption structure on top of the Si dimer.

Using density-functional theory and cluster models, Musgrave and coworkers[21–24] studied the reaction of various organics (containing the alkene,[21] the nitrile,[22,23] and the ketone[24] functional groups) on the Si(001) and Ge(001) surfaces. They found that the reaction products of organics on Si(001) are almost irreversibly stable on the surface whereas

certain reactions occurring on Si(001) may be less favorable or even inaccessible on Ge(001) due to relatively weaker bondings of organics on Ge(001). Hence, thermodynamic factors tend to play critical roles on the reaction of some organics on Ge(001).

In order to find a chemically subtle difference in the adsorption of the unsaturated hydrocarbons on Si(001) and Ge(001), we here present first-principles calculations for the adsorption energies (E_{ads}) of C_2H_2, C_2H_4, and C_6H_6 on the Si(001) and Ge(001) surfaces. In this study we consider only one adsorption structure (i.e., the so-called di-σ structure, see Fig. 1) which was commonly observed in the adsorption of the three unsaturated hydrocarbons on Si(001) and Ge(001), therefore their bonding strengths can be compared on the equal ground.

We perform the total-energy and force calculations using density-functional theory[25] within the generalized-gradient approximation[26] (GGA). We use the exchange-correlation functional of Perdew *et al.*[26] for the GGA. The norm-conserving pseudopotentials of Si and H atoms were constructed by the scheme of Troullier and Martins[27] in the separable form of Kleinman and Bylander.[28] For C atom whose $2s$ and $2p$ valence orbitals are strongly localized, we used the Vanderbilt ultrasoft pseudopotential.[29] The surface is modeled by a periodic slab geometry. Each slab contains five Si (Ge) atomic layers plus adsorbed molecules and the bottom Si (Ge) layer is passivated by two H atoms per Si (Ge) atom. The thickness of the vacuum region between these slabs is about 10 Å. A plane-wave basis set was used with 25 Ry cutoff, and the **k** space integration was done with meshes of four **k** points in the 2×2 surface Brillouin zones. All the atoms except the bottom Si or Ge layer were allowed to relax

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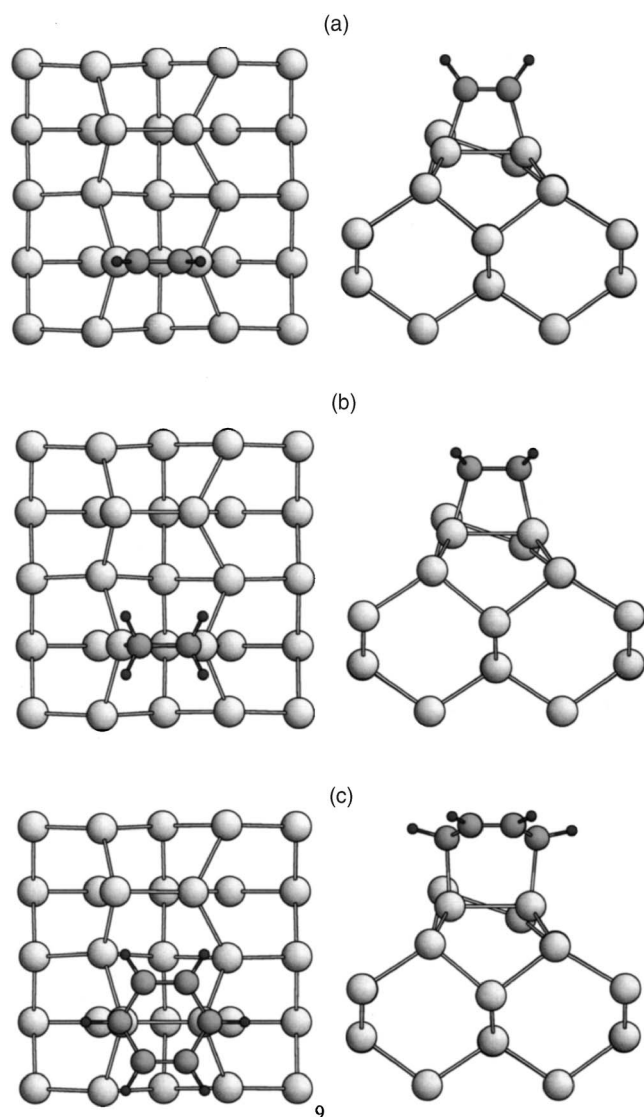
(a)

(b)

(c)

9

FIG. 1. Top and side views of the optimized structure of adsorbed (a) C_2H_2, (b) C_2H_4, and (c) C_6H_6 on Ge(001). The large, medium, and small circles represent Ge, C, and H atoms, respectively.

TABLE I. Calculated adsorption energies of C_2H_2, C_2H_4, and C_6H_6 on Si(001) and Ge(001), in comparison with the desorption energies obtained by TPD experiments. The calculated bond lengths between the C atom and its bonded Si or Ge atom are also given.

		C_2H_2	C_2H_4	C_6H_6
Si(001)	E_{ads}(eV)	2.74	1.94	0.82
	E_{des}(eV)	2.0[a]	1.8[b]	1.2[c]
	d_{C-Si}(Å)	1.91	1.95	1.98
Ge(001)	E_{ads}(eV)	1.78	1.07	0.06
	E_{des}(eV)	1.4[a]	1.1[b]	0.5[c]
	d_{C-Ge}(Å)	2.02	2.07	2.12

[a]Reference 9.
[b]Reference 16.
[c]Reference 17.

electron density along the C—Ge bond locates around the bonded C atom because of its higher electronegativity compared with that of the Ge atom. Thus, we can say that the bonding nature of C_2H_2, C_2H_4, and C_6H_6 on Ge(001) [also on Si(001)] is ionic. This ionic nature of the C—Si (C—Ge) bond on the Si (Ge) surface decreases in strength as the sequence of $C_2H_2 > C_2H_4 > C_6H_6$, yielding $E_{ads}(C_2H_2) > E_{ads}(C_2H_4) > E_{ads}(C_6H_6)$. We note that the contour line of 0.24 electrons/bohr^3 encircles adsorbed C_2H_2, while in adsorbed C_2H_4 it does not. This indicates that the ionic nature of the C—Ge bond in C_2H_2 adsorption is greater than that in C_2H_4 adsorption. For adsorbed C_6H_6 the diminution of the valence electron charge is seen along the C—Ge bond where the 0.24 electrons/bohr^3 contour, present in adsorbed C_2H_4, is missing. This can be related with a relatively weaker bonding of C_6H_6 on Ge(001).

The above sequence of the ionic nature (or bonding strength) among the three unsaturated hydrocarbons on the Si (Ge) surface can be reflected by the bond length d_{C-Si} (d_{C-Ge}) between the C atom and its bonded Si (Ge) atom. The calculated bond lengths are listed in Table I. We find that d_{C-Si} (d_{C-Ge}) is 1.91 (2.02), 1.95 (2.07), 1.98 (2.12) Å for adsorbed C_2H_2, C_2H_4, and C_6H_6 on the Si (Ge) surface, respectively. This increase of d_{C-Si} (d_{C-Ge}) among the three adsorbed molecules is in accord with the decrease of their adsorption energies on the Si (Ge) surface.

Acetylene, ethylene, and benzene containing a C≡C triple bond, a C=C double bond, or a π-conjugated aromatic ring have the bond orders of 3, 2, and 1.5, respectively. It is interesting to note that the decrease of binding energy in going from bond order 3 to 2 (i.e., the bond order change of 1) is similar to the change from bond order 2 to 1.5 (i.e., the bond order change of 0.5). However, we have to notice that there may be other effects involved in determining the binding energies of the three molecules. The strain in the four-membered or six-membered ring formed in acetylene, ethylene, and benzene adsorptions is possibly different from each other. For example, upon adsorption the geometry of benzene is largely distorted from its planar molecular structure [see Fig. 1(c)]. The steric interactions of the H atoms with the surface would be also different between the three cases.

It is well known that the bonding of organic molecules to Ge(001) is much weaker than to Si(001).[21–24,30,31] In the

along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr.

We optimize the atomic structure of adsorbed acetylene, ethylene, and benzene on Si(001) and Ge(001) using a (2×2) unit cell which involves two alternating buckled dimers. Each optimized structure on Ge(001) is shown in Fig. 1 and its adsorption energy is given in Table I. We find that the adsorption energies for adsorbed C_2H_2, C_2H_4, and C_6H_6 on the Si (Ge) surface are 2.74 (1.78), 1.94 (1.07), and 0.82 (0.06) eV, respectively, showing a large difference of stabilities between organics with different types of π bonds. This result indicates that C_2H_2 containing the triple bond more strongly bonds to the surface dimer compared with C_2H_4 containing the double bond, while C_6H_6 containing the aromatic ring is the weakest bonding to the surface dimer.

To examine the bonding nature of the three unsaturated hydrocarbons on Si(001) and Ge(001), we calculate the valence electron density for each adsorption structure. The charge-density plots on Ge(001) are displayed in Fig. 2. We see in all the three adsorbed molecules that the high valence
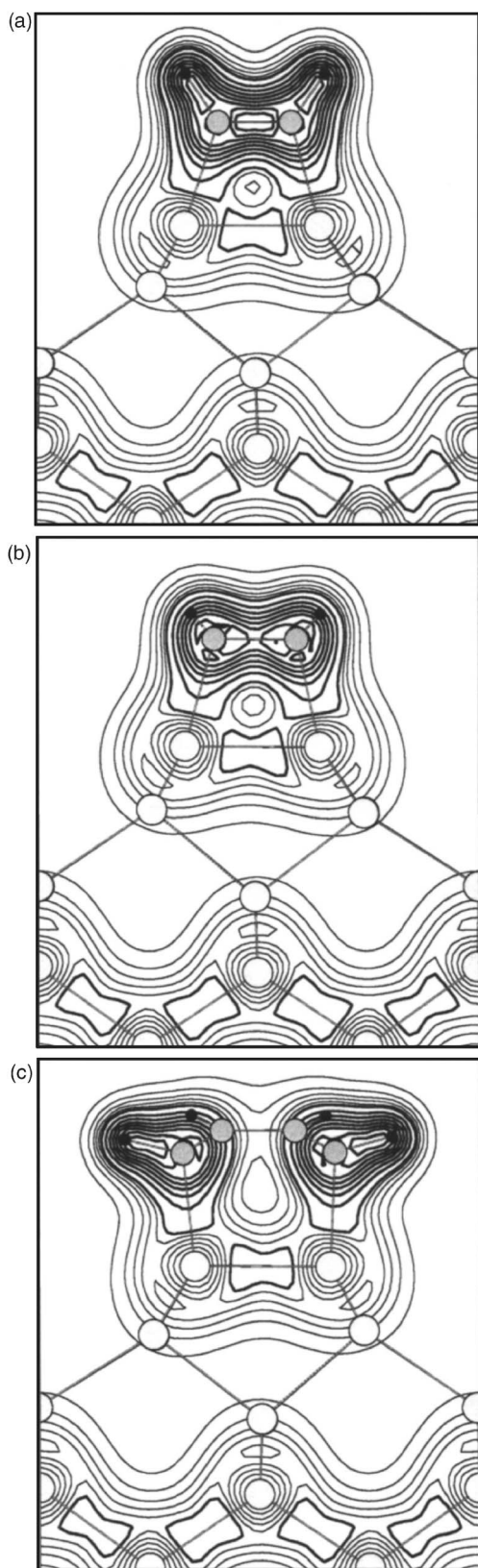
(a)

(b)

(c)

FIG. 2. Calculated charge densities for adsorbed (a) C_2H_2, (b) C_2H_4, and (c) C_6H_6 on Ge(001). Two kinds of contour spacings are used. The first thin line is at 0.01 electron/bohr^3 with spacings of 0.01 electron/bohr^3 and the first thick line is at 0.06 electron/bohr^3 with a spacing of 0.03 between thick lines. The plots are drawn in a vertical plane containing the Ge dimer.

present study the adsorption energy difference (ΔE_{ads}) of C_2H_2, C_2H_4, and C_6H_6 between Si(001) and Ge(001) amounts to 0.96, 0.87, and 0.76 eV, respectively. Interestingly, ΔE_{ads} decreases as the order of $\Delta E_{ads}(C_2H_2)$ $> \Delta E_{ads}(C_2H_4) > \Delta E_{ads}(C_6H_6)$. Noting that (i) the calculated dimer bond lengths (d_{dimer}) of Si(001) and Ge(001) are 2.36 and 2.58 Å, and (ii) the calculated C—C bond lengths (d_{C-C}) of C_2H_2, C_2H_4, and C_6H_6 (C_1–C_4 atoms) molecules are 1.20, 1.34, 2.81 Å, it is likely that C_6H_6 adsorption in which $d_{C_1-C_4}$ is the most comparable to d_{dimer} has the smallest ΔE_{ads}.

Here, all the adsorption systems except C_6H_6/Ge(001) have sufficient adsorption energies to be classified as chemisorption. In contrast to chemisorbed C_6H_6 on Si(001), C_6H_6 weakly bonds to Ge(001). This disparate features of C_6H_6 adsorption on Si(001) and Ge(001) provide an explanation for temperature-programed desorption (TPD) data of Fink *et al.*[17] where about 60% (40%) of adsorbed C_6H_6 molecules on Ge(001) consists of a weakly (strongly) bound species while on Si(001) the weakly bound species is absent and the saturated benzene monolayer is composed of the chemisorption state. In the present study we are unable to suggest the adsorption configurations for the two observed[17] states in the C_6H_6/Ge(001) system. However, we can say that the presence of the weakly bound state is possibly caused by a decreased bonding strength between C_6H_6 and the Ge dimer, whereas the chemisorption state may be interpreted in terms of a different adsorption configuration we have not considered or as due to adsorption at step sites as suggested by Fink *et al.*[17]

Our calculated adsorption energies are compared with the desorption energies (E_{des}) obtained by TPD experiments (see Table I).[9,16,17] The absolute values of both quantities somewhat largely differ from each other except those of C_2H_4 adsorption. However, ΔE_{ads} of C_2H_2, C_2H_4, and C_6H_6 between Si(001) and Ge(001) is similar to the corresponding difference of E_{des} which amounts to ~0.7 eV.

Previous density-functional theory calculations[32] found that the adsorbed cyclopentene (C_5H_8) on Si(001) and Ge(001) has E_{ads}=1.63 and 0.79 eV, respectively (i.e., 0.84 eV lower in Ge). By adsorption on Si(001) and Ge(001), cyclopentene has a slightly larger strain, due to the ring, than the ethylene. Thus, the adsorption energies are slightly reduced (by 0.31 on Si and 0.28 eV on Ge) than those of the ethylene. Note that upon adsorption the planar geometry of the free C_5 pentagon becomes buckled while forming tetrahedral bonds with the Si or Ge dimer atoms.[32] In addition, adsorbed 1,4-cyclohexadiene on Si(001) whose adsorption energy for the di-σ structure was previously[33] calculated to be 1.31 eV, which is smaller than those of ethylene and cyclopentene (by 0.63 and 0.32 eV, respectively). This implies that the adsorbed 1,4-cyclohexadiene, due to the presence of two double bonds, has more strain than the adsorbed cyclopentene. Given the systematic decrease of the adsorption energy of the unsaturated hydrocarbons on Ge(001) with respect to Si(001) (by 0.96, 0.87, and 0.76 eV for triple, double, and aromatic bonds, respectively), the expected adsorption energy for 1,4-cyclohexadiene on Ge(001) is

~0.5 eV. Indeed, we obtain $E_{ads}=0.47$ eV for the optimized structure of adsorbed 1,4-cyclohexadiene on Ge(001).

In summary, we have performed first-principles density-functional calculations for the adsorption of C_2H_2, C_2H_4, and C_6H_6 on Si(001) and Ge(001). We found that as the C—C bond order of unsaturated hydrocarbon molecule increases, its bonding to the surface dimer is enhanced as a consequence of the increased ionic bonding nature. The present theory provides useful information about the bonding and binding of various unsaturated hydrocarbons on the two representative semiconductor surfaces, Si(001) and Ge(001).

[1] R. A. Wolkow, Annu. Rev. Phys. Chem. **50**, 413 (1999).

[2] S. F. Bent, Surf. Sci. **500**, 879 (2002), and references therein.

[3] Q. Liu and R. J. Hoffmann, J. Am. Chem. Soc. **117**, 4082 (1995).

[4] R. Konečny and D. J. Doren, Surf. Sci. **417**, 169 (1998).

[5] D. C. Sorescu and K. D. Jordan, J. Phys. Chem. **104**, 8259 (2000).

[6] S. Mezhenny, I. Lyubinetsky, W. J. Choyke, R. A. Wolkow, and J. T. Yates, Jr., Chem. Phys. Lett. **344**, 7 (2001).

[7] W. Kim, H. Kim, G. Lee, Y. K. Hong, K. Lee, C. Hwang, D. H. Kim, and J. Y. Koo, Phys. Rev. B **64**, 193313 (2001).

[8] Y. Morikawa, Phys. Rev. B **63**, 033405 (2001).

[9] A. Kim, J. Y. Maeng, J. Y. Lee, and S. Kim, J. Chem. Phys. **117**, 10215 (2002).

[10] J.-H. Cho and L. Kleinman, Phys. Rev. B **69**, 075303 (2004).

[11] L. Clemen, R. M. Wallace, P. A. Taylor, M. J. Dresser, W. J. Choyke, W. H. Weinberg, and J. T. Yates, Jr., Surf. Sci. **268**, 205 (1992).

[12] A. J. Mayne, A. R. Avery, J. Knall, T. S. Jones, G. A. D. Briggs, and W. H. Weinberg, Surf. Sci. **284**, 247 (1993).

[13] H. Liu and R. J. Hamers, J. Am. Chem. Soc. **119**, 7593 (1997).

[14] F. Matsui, H. W. Yeom, A. Imanishi, K. Isawa, I. Matsuda, and T. Ohta, Surf. Sci. **401**, L413 (1998).

[15] R. Terborg, P. Baumgärtel, R. Lindsay *et al.*, Phys. Rev. B **61**, 16697 (2000).

[16] A. Fink, R. Huber, and W. Widdra, J. Chem. Phys. **115**, 2768 (2001).

[17] A. Fink, D. Menzel, and W. Widdra, J. Phys. Chem. B **105**, 3828 (2001).

[18] G. P. Lopinski, D. J. Moffatt, and R. A. Wolkow, Chem. Phys. Lett. **282**, 305 (1998).

[19] B. Borovsky, M. Krueger, and E. Ganz, Phys. Rev. B **57**, R4269 (1998).

[20] W. A. Hofer, A. J. Fisher, G. P. Lopinski, and R. A. Wolkow, Phys. Rev. B **63**, 085314 (2001).

[21] C. Mui, S. F. Bent, and C. B. Musgrave, J. Phys. Chem. A **104**, 2457 (2000).

[22] C. Mui, M. A. Filler, S. F. Bent, and C. B. Musgrave, J. Phys. Chem. B **107**, 12256 (2003).

[23] M. A. Filler, C. Mui, C. B. Musgrave, and S. F. Bent, J. Am. Chem. Soc. **125**, 4928 (2003).

[24] G. T. Wang, C. Mui, C. B. Musgrave, and S. F. Bent, J. Am. Chem. Soc. **124**, 8990 (2002).

[25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[26] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[27] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[28] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[29] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *ibid.* **47**, 10142 (1993).

[30] G. T. Wang, C. Mui, C. B. Musgrave, and S. F. Bent, J. Am. Chem. Soc. **124**, 8990 (2002).

[31] R. Miotto, A. C. Ferraz, and G. P. Srivastava, Surf. Sci. **507**, 12 (2002).

[32] J.-H. Cho and L. Kleinman, Phys. Rev. B **67**, 115314 (2003).

[33] J.-H. Cho, D. Oh, K. S. Kim, and L. Kleinman, J. Chem. Phys. **116**, 3800 (2002).