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First-principles study of the adsorption and reaction of cyclopentene on Ge(001)

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The adsorption and reaction of cyclopentene on the Ge(001) surface is investigated by first-principles density-functional calculations within the generalized gradient approximation. Surprisingly, a recent cluster calculation for adsorbed cyclopentene on Ge(001) obtained an adsorption energy of 2.10 eV, which is larger than the same cluster result (1.65 eV) on Si(001). However, our calculated adsorption energy for 0.5(1)-monolayer cyclopentene on Ge(001) is 0.79(0.51) eV, comparable with an observed activation energy of 0.7 eV for desorption. In addition we find that the energy barriers for the adsorption of cyclopentene on Ge(001) and Si(001) not only depend on cyclopentene coverage but also quantitatively differ from each other. Based on the calculated energy profile for the reaction we discuss the experimental observations of the difference between cyclopentene sticking on the Ge(001) and Si(001) surfaces.

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Over the past several years the adsorption of unsaturated hydrocarbon molecules on semiconductor surfaces has attracted much attention because of the technological interest of combining the wide range of functionality of organic molecules with the existing semiconductor-based infrastructure.[1–4] Especially the Si(001) surface has been extensively employed for the investigation of hybrid organic-silicon systems,[5–16] whereas only little work addressed hydrocarbon adsorbates on the Ge(001) surface.[17–20] There is a general consensus that the reaction of unsaturated hydrocarbons (e.g., alkenes) with Si(001) takes place via a precursor state, finally forming a $[2+2]$ product in which the π bond of alkene and the π bond of a surface dimer interact to produce two σ bonds.[8,10,13,14] Although the reaction mechanisms of unsaturated hydrocarbons on Si(001) and Ge(001) are expected to be similar to each other because of the same surface reconstruction, it is interesting to point out that there is a chemically subtle difference in the adsorption kinetics on the two surfaces. For example, Hamers and co-workers reported that the sticking coefficient of cyclopentene on Ge(001) is considerably reduced compared with that on Si(001).[11,17]

It has been known that the binding of unsaturated hydrocarbons on Ge(001) is weaker than that on Si(001).[17–20] A cluster calculation[18] for adsorbed 1,3-butadiene on Si(001) and Ge/Si(001) showed that the C-Si bond is stronger than the C-Ge bond by $\sim$0.43 eV. Using temperature-programmed desorption (TPD) spectroscopy Fink, Menzel, and Widdra[19] found that the desorption temperature of chemisorbed benzene on Ge(001) is about 230 K, which is much lower than the 430 K on Si(001). This observation indicates that benzene binding on Ge(001) is weak compared to that on Si(001). In contrast, a recent cluster calculation[17] for adsorbed cyclopentene on Ge(001) obtained an adsorption energy of 2.10 eV, which is greater than the same cluster result (1.65 eV) of adsorbed cyclopentene on Si(001). This value on Ge(001) is far off a desorption activation energy (0.7 eV) measured with a TPD experiment.[17] In their scanning-tunneling-microscopy (STM) study Lee *et al.*[17] found that at room temperature an exposure of Si(001) to 0.1 Langmirs (L) of cyclopentene led to $\sim$0.1 ML coverage, while 10 L was needed to produce the comparable surface coverage of cyclopentene on Ge(001). From this they estimated that the sticking coefficient of cyclopentene is lower on Ge(001) by a factor of 10 compared to a unity value on Si(001). (We do not understand why the factor is not 100.) Our previous study[16] for adsorbed cyclopentene on Si(001) found that there is a large repulsive hydrogen-hydrogen interaction between the nearby adsorbed molecules. Interestingly, despite a $\sim$4% larger lattice constant of Ge compared to Si, the highest packing of cyclopentene on Ge(001) was observed to be two adsorbed cyclopentene molecules for every three Ge dimers, which is less than the nearly well-ordered 1 ML packing on Si(001).[11,17]

In this paper we study not only the binding energy and structure of adsorbed cyclopentene on Ge(001), but also the kinetics of cyclopentene adsorption using first-principles density-functional theory calculations. We find that a cyclopentene molecule weakly bonds to the Ge dimer, with a relatively small binding energy compared to the case on Si(001). In both systems a repulsive H-H interaction between cyclopentene molecules adsorbed on neighboring sites exists, drastically affecting the adsorption kinetics with increasing coverage. On Ge(001) the calculated energy barrier $E_{\mathrm{b}}(P\text{-}C)$ from the precursor state to the chemisorption state within the coverage of $\theta=0.5$ ML is 0.38 eV, which is greater than the adsorption energy $[E_{\mathrm{ads}}(P)=0.26\ \mathrm{eV}]$ of the precursor state. On the other hand, on Si(001) the corresponding $E_{\mathrm{ads}}(P)$ and $E_{\mathrm{b}}(P\text{-}C)$ are calculated to be 0.41 and 0.08 eV respectively. These quantitatively different energy profiles of the reaction path between Ge(001) and Si(001) explain the experimental observations[11,17] that the sticking coefficient of cyclopentene on Ge(001) is much reduced compared with a unity value on Si(001). Above $\theta=0.5$ ML the precursor state on both Ge(001) and Si(001) surfaces is found to be higher in energy than the gas state, possibly due to the repulsive H-H interaction between the nearby adsorbed molecules. This result predicts that the sticking coefficient should decrease at high coverages above 0.5 ML, as observed in the TPD experiment.[17]

The total-energy and force calculations were carried out using density-functional theory[21] within the generalized-gradient approximation.[22] The C (Ge, Si, and H) atom is

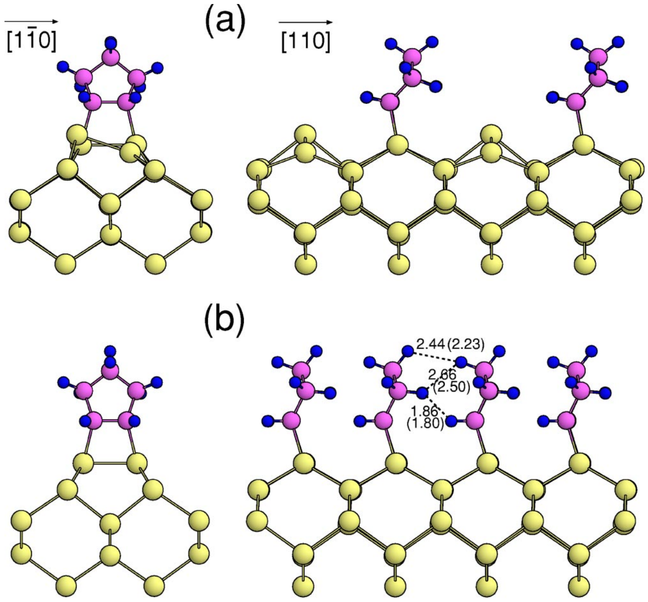

FIG. 1. Optimized structure of adsorbed cyclopentene on Ge(001) with the coverages of (a) 0.5 ML and (b) 1 ML. The two side views from the [110] and $[1\bar{1}0]$ directions are displayed. The numbers in (b) denote the H-H interatomic distances (in Å) between the nearby adsorbed cyclopenten molecules. For comparison the values on Si(001) are given in parentheses.

described by ultrasoft[23] (norm-conserving[24]) pseudopotentials. The surface is modeled by a periodic slab geometry. Each slab contains five Ge (Si) atomic layers plus adsorbed cyclopentene molecules and the bottom Ge (Si) layer is passivated by two H atoms per Ge (Si) atom. The thickness of the vacuum region between these slabs is about 10 Å. A plane-wave basis set was used with a 25-Ry cutoff, and the **k**-space integration was done with meshes of eight and four **k** points in the (2×1) and (2×2) surface Brillouin zones, respectively. All the atoms except the bottom Ge or Si layer were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr.

We first determine the atomic structure of adsorbed cyclopentene on Ge(001) for coverages of $\theta=0.5$ and 1 ML. The optimized structures for both coverages are shown in Figs. 1(a) and 1(b), respectively. The calculated adsorption energies are given in Table I, together with our present and previous[16] results for adsorbed cyclopentene on Si(001). On Ge(001) we find an adsorption energy of 0.79 (0.51) eV for $\theta=0.5$ (1) ML, in accordance with a desorption energy of 0.7 eV measured using TPD spectroscopy.[17] The smaller adsorption energy at $\theta=1$ ML is attributed to the repulsive H-H interaction between the nearby adsorbed cyclopentene molecules. As shown in Fig. 1(b), the H-H interatomic distances ($d_{\text{H-H}}$) are in the range between 1.86 and 2.66 Å. We note that the adsorption energy difference $\Delta E_{\text{ads}}=0.28$ eV between $\theta=0.5$ and 1 ML is smaller than the corresponding one ($\Delta E_{\text{ads}}=0.43$ eV) on Si(001), where the calculated adsorption energy for $\theta=0.5(1)$ ML is 1.63(1.20) eV.[25] This result reflects that the H-H repulsion on Ge(001) is weaker than on Si(001) because of the relatively longer values of $d_{\text{H-H}}$ [see Fig. 1(b)].

TABLE I. Calculated adsorption energies of cyclopentene on Ge(001) and Si(001) with the coverages of 0.5 and 1 ML, in comparison with those of a cluster calculation. *P* indicates the precursor state. The values in parentheses represent our previous (Ref. 16) results for the cyclopentene/Si(001) system which was simulated with cyclopentene molecules adsorbed on both sides of a 12 Si atomic-layer slab.

	Coverage	E_{ads} (eV)
cyclopentene/Ge(001)	cluster [a]	2.10
	present—0.5 ML	0.79
	present—1 ML	0.51
	present—0.5 ML *P*	0.26
	present—1 ML *P*	−0.02
cyclopentene/Si(001)	cluster [a]	1.65
	present—0.5 ML	1.63(1.60)
	present—1 ML	1.20(1.17)
	present—0.5 ML *P*	0.41
	present—1 ML *P*	−0.20(−0.22)

[a] References 17.

In Table I we see that our calculated adsorption energy of cyclopentene on Ge(001) is smaller than that on Si(001) by 0.84(0.69) eV for $\theta=0.5(1)$ ML, showing that the bonding of cyclopentene to Ge(001) is significantly weaker than that on Si(001). This weaker binding of cyclopentene on Ge(001) is consistent with other hydrocarbon cases such as ethylene,[20] benzene,[19] and 1,3-butadiene.[18] In contrast, a recent cluster calculation carried out by Lee *et al.*[17] found that adsorbed cyclopentene on Ge(001) has a relatively larger adsorption energy of 2.10 eV compared to that ($E_{\text{ads}}=1.65$ eV) on Si(001). For the cyclopentene/Si(001) system the adsorption energy obtained from the cluster calculation[17] agrees well with our value of 1.63 eV (for $\theta=0.5$ ML). Here the cluster results for the structural parameters such as the bond lengths and bond angles are very close to the present ones (see Table II). However, for the cyclopentene/Ge(001) system the adsorption energy as well as the bond lengths and bond angles show large differences between the cluster[17] and the present calculations. Especially the differences of the bond lengths $d_{\text{Ge-Ge}}$ and $d_{\text{Ge-C}}$ (0.10 and 0.08 Å, respectively) are significant. Noting that our Ge adsorption energies are close to Lee *et al.*'s measured desorption activation energy, it seems that the description of Ge atoms in their cluster calculation[17] might have a problem.

Similar to the cases of acetylene[8,9] and ethylene,[6] the reaction of cyclopentene[11] with Si(001) was found to be facile with a nearly unity sticking coefficient at room temperature.[11] However, using STM Lee *et al.*[17] observed that at a low coverage of ~0.1 ML the sticking coefficient of cyclopentene on Ge(001) decreases by a factor of 10 or 100 compared with that on Si(001). In order to understand the difference of cyclopentene sticking on the Ge(001) and Si(001) surfaces, we study the reaction path for the adsorption via the precursor state (the so-called "three-atom" intermediate state) which is composed of a three-membered ring with the two C atoms [C_1 and C_2 in Fig. 2(a)] and the down Ge atom (in Ge dimer). This precursor state is expected to be

TABLE II. Calculated bond lengths and bond angles of adsorbed cyclopentene on Ge(001) and Si(001) in comparison with the cluster data. X denotes Ge or Si surface dimer atoms.

		$d_{\text{C-C}}$ (Å)	$d_{X\text{-}X}$ (Å)	$d_{X\text{-C}}$ (Å)	$\phi_{X\text{-C-C}}$ (°)	$\phi_{\text{C-}X\text{-}X}$ (°)
cyclopentene/Ge(001)	cluster [a]	1.58	2.41	2.00	101.9	78.1
	present—0.5 ML	1.56	2.51	2.08	104.4	75.6
	present—1 ML	1.56	2.51	2.08	103.2	76.7
cyclopentene/Si(001)	cluster [a]	1.59	2.36	1.95	101.3	78.7
	present—0.5 ML	1.58	2.37	1.96	102.3	79.1
	present—1 ML	1.58	2.38	1.97	101.8	78.3

[a] References 17.

easily produced because of the energetically favored hybridization between the π bonding state of unsaturated hydrocarbons and the empty dangling-bond state of the down Ge atom. We find on Ge(001) that the precursor state [Fig. 2(a)] is stabilized over the gas state by 0.26 eV in adsorption energy. To find the energy barrier from the precursor state to the chemisorption state [Fig. 2(c)], we used the 2×2 unit cell with $\theta=0.5$ ML. We constrained the midpoint between the C_1 and C_2 atoms to lie along the line connecting its position in the precursor and chemisorption states. At each of several points along this line we relaxed all the atoms to their equilibrium positions, enforcing the constraint by relaxing C_1 and C_2 in opposite directions along the calculated Hellmann-Feynman forces $\pm(\mathbf{F}_1-\mathbf{F}_2)/2$. At the transition state $\mathbf{F}_1$ and $\mathbf{F}_2$ were each negligible. The calculated energy profile and the atomic geometries at the precursor, transition, and chemisorption states are displayed in Fig. 2. The energy barrier from the precursor state to the chemisorption state is $E_{\text{b}}=0.38$ eV, greater than $E_{\text{ads}}=0.26$ eV of the precursor state. Using an Arrhenius-type activation process with a typical value[26] ($\sim10^{14}$ Hz) for the preexponential factor, we estimate that at room temperature the reaction rate for the chemisorption from the precursor state is $\sim4.2\times10^{7}$ s^{-1} which is smaller than the desorption rate of $\sim4.4\times10^{9}$ s^{-1} by a factor of about 100. Thus we can say that the desorption of cyclopentene from the precursor state is easily activated, accompanied by a very small portion ($\sim1\%$) of chemisorption. This aspect for the reaction of cyclopentene with Ge(001) results in low sticking, as observed in the STM and TPD experiments.[17] On the other hand, on Si(001) the thermal activation from the precursor state to the chemisorption state easily takes place because of a shallow energy barrier of $E_{\text{b}}=0.08$ eV while $E_{\text{ads}}=0.41$ eV for the precursor state (see the dashed line in Fig. 2), leading to an observed unity sticking coefficient.[11]

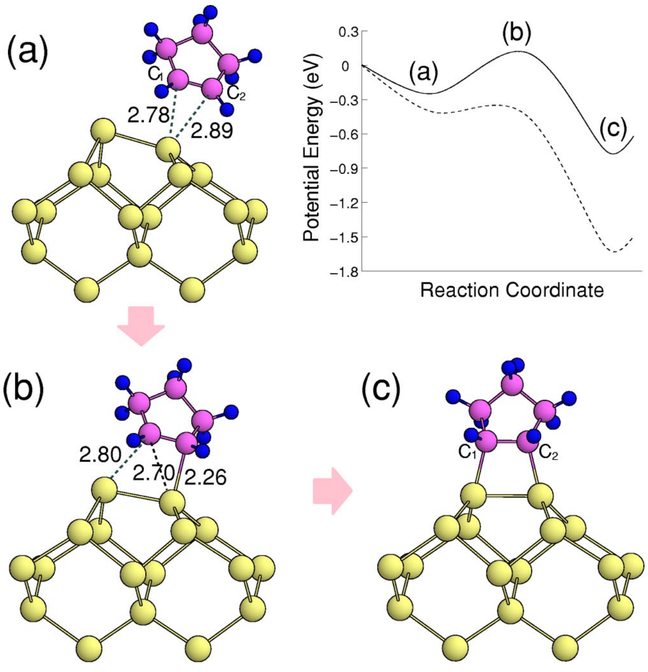

FIG. 2. Calculated energy profile (solid line) for the reaction of cyclopentene on Ge(100). The atomic geometries of the three representative points are given: (a) the precursor state, (b) the transition state, and (c) the chemisorption state. The dashed line represents the energy profile for cyclopentne on Si(001). Energy is referenced from the gas state.

From the TPD spectra of cyclopentene on Ge(001) Lee *et al.*[17] found that the slope of the uptake curve decreases with increasing exposure, indicating that the sticking coefficient decreases as the coverage of cyclopentene increases. As a matter of fact, our previous study[16] for adsorbed cyclopentene on Si(001) showed that above $\theta=0.5$ ML the precursor state is less stable than the gas state by 0.22 eV, producing a significantly reduced adsorption rate compared to that below 0.5 ML where the precursor state is more stable than the gas state. Similarly, on Ge(001) the formation of the precursor state above $\theta=0.5$ ML has an energy 0.02 eV higher than the gas state (see Table I). This relatively enhanced stability of the precursor state on Ge(001) compared to that on Si(001) is possibly due to a decreased H-H repulsive interaction between the nearby adsorbed molecules. Consequently, we expect that above $\theta=0.5$ ML the sticking coefficient of cyclopentene on Ge(001) is rather higher than that on Si(001).

It is noticeable that upon annealing the chemisorbed cyclopetene on Ge(001) with $\theta=1$ ML can easily desorb into the gas state because of its weak adsorption energy ($E_{\text{ads}}=0.51$ eV). The reaction rate for the desorption is estimated as $\sim2.8\times10^{5}$ s^{-1} at room temperature, indicating an easy thermal activation. Thus we believe that this causes some frequently observed vacant sites on Ge(001).[17] On the other hand, on Si(001) such a desorption is not expected at room temperature because of the large adsorption energy of 1.20 eV and therefore a relatively well-ordered packing of cyclopentene can be preserved at room temperature, as observed in the STM experiment.[11]

In summary, our first-principles density-functional calculations showed that the bonding of cyclopentene molecules to Ge(001) is much weaker than to Si(001), in agreement with Lee *et al.*'s experiment but not their cluster calculation.[17] We found that the stability of the precursor state is sensitive to the coverage of cyclopentene due to the repulsive H-H interaction between the nearby adsorbed molecules. At the coverage of $\theta = 0.5$ (1) ML the precursor state on both Ge(001) and Si(001) surfaces is found to be more (less) stable compared to the gas state, indicating a significant change of the sticking coefficient with increasing coverage. Our calculated energy profile for the reaction path predicts that below $\theta = 0.5$ ML the sticking coefficient on Ge(001) is lower than that on Si(001), but above 0.5 ML this would be reversed.

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[1] J.T. Yates, Jr., Science **279**, 335 (1998).

[2] M. Jacoby, Chem. Eng. News **78**, 32 (2000).

[3] R.A. Wolkow, Annu. Rev. Phys. Chem. **50**, 413 (1999), and references therein.

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

[5] M. Nishijima, J. Yoshinobu, H. Tsuda, and M. Onchi, Surf. Sci. **192**, 383 (1987).

[6] 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).

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

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

[9] L. Li, C. Tindall, O. Takaoka, Y. Hasegawa, and T. Sakurai, Phys. Rev. B **56**, 4648 (1997).

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

[11] R.J. Hamers, J.S. Hovis, S. Lee, H. Liu, and J. Shan, J. Phys. Chem. **101**, 1489 (1997); J.S. Hovis, H. Liu, and R.J. Hamers, Surf. Sci. **402**, 1 (1998).

[12] J.S. Hovis and R.J. Hamers, J. Phys. Chem. **101**, 9581 (1997).

[13] C.H. Choi and M.S. Gordon, J. Am. Chem. Soc. **121**, 11311 (1999).

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

[15] K. Hamaguchi, S. Machida, M. Nagao, F. Yasui, K. Mukai, Y. Yamashita, J. Yoshinobu, H.S. Kato, H. Okuyama, M. Kawai, T. Sato, and M. Iwatsuki, J. Phys. Chem. **105**, 3718 (2001).

[16] J.-H. Cho and L. Kleinman, Phys. Rev. B **64**, 235420 (2001).

[17] S.W. Lee, J.S. Hovis, S.K. Coulter, R.J. Hamers, C.M. Greenlief, Surf. Sci. **462**, 6 (2000).

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

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

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

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

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

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

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

[25] For the cyclopentene/Si(001) system the present calculation increases the adsorption energy by 0.03 eV compared to the result of Ref. 16 (see Table I). In the present and previous calculations the energy difference between the chemisorption and precursor states changes only by 0.01 eV. The small differences between our current and previous results arise from the fact that previously we were not making tedious reaction pathway calculations and thus could afford to use a much thicker Si film.

[26] R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces* (Wiley, New York, 1996), p. 607.