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Ab initio calculations of cyclopentene adsorbed on the diamond (001) surface

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We study cyclopentene adsorbed on the diamond (001) surface by first-principles density-functional calculations within the generalized-gradient approximation. Unlike Si(001), which attains full cyclopentene coverage with a (2×1) surface unit cell, we find that diamond can attain only half coverage with a $c(4\times2)$ unit cell yielding 0.86-eV (per adsorbed cyclopentene) more adsorption energy than a $p(2\times2)$ unit cell.

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I. INTRODUCTION

Organic-semiconductor hybrid materials provide a favorable linking of organic chemistry to existing semiconductor-based microelectronic technologies, and therefore the useful properties of organic molecules such as light emission or light detection may be tailored to semiconductor-based devices.[1,2] Recently, several experimental groups[3–5] have demonstrated the formation of organic nanostructures on the Si(001) surface, and further expanded such hybridization with the diamond (001) surface[6,7] which has various useful material properties including high thermal conductivity, chemical inertness, hardness, and a wide band gap.

The (001) surfaces of silicon and diamond exhibit the same (2×1) surface reconstruction in which pairs of surface atoms bond to each other with a strong σ bond and a weak π bond, leading to dimers.[8] As a result, it is expected that the reaction of organic molecules with these surfaces might show a similarity. Recently, Hamers and his co-workers[3,6] studied the adsorption of cyclopentene (C_5H_8) on both Si(001) and C(001) using Fourier-transform infrared (FTIR) spectroscopy, scanning tunneling microscopy (STM), and x-ray photoelectron spectroscopy techniques. The reaction between cyclopentene and these (001) surfaces has been explained by the so-called [2+2] cycloaddition mechanism[3,6] where the interaction of the π bond of unsaturated hydrocarbons (cyclopentene in this case) with the π bond of a dimer produces two new σ bonds (see Fig. 1). Interestingly, the adsorption of cyclopentene on C(001) has a very low sticking coefficient (~0.001), contrasting with a nearly unity value up to half coverage on Si(001). For this low sticking coefficient for cyclopetene on C(001) Hovis *et al.*[6] claimed that the symmetric dimer structure of C(001) may induce a high reaction barrier, together with the electronic and bonding properties of C(001), such as a larger $\pi-\pi^*$ surface-state band gap and a stronger π bond compared with those of the Si(001) surface. Note that on Si(001) the reaction pathway for the [2+2] product predicts little or no barrier[3,9] through a low-symmetry intermediate state because of the asymmetric Si dimer structure. However, Carbone[10] argued that the large dose of ~5000 L required[6] to saturate the C(001) surface with cyclopentene indicates the adsorption could [analogous to oxygen[11,12] on Si(001)-2×1] take place on defects rather than on diamond dimers. Hovis *et al.*[13] responded to this comment by pointing out that the infrared spectrum of cyclopentene on diamond is very similar to that obtained on Ge and Si(001) surfaces, for which STM images clearly show reaction with the Si dimers. They also argue that they found a uniform increase in infrared absorption as the exposure is increased up to a final value that is close to ‘‘monolayer’’ coverage. If adsorption occurred only on defects, absorption would saturate quickly with exposure to a very weak value.

We do not study the adsorption kinetics of cyclopentene on C(001) but only the binding energy and structure for several possible saturated surfaces. We agree with Hovis *et al.*'s interpretation of their data except that we find the surface is saturated at half coverage (full coverage, $\theta=1$ ML, is defined as one molecule per surface dimer). Our results show that cyclopentene molecules strongly adsorb on C dimers, with a relatively larger adsorption energy compared to that on Si(001). However, significant repulsive interactions between adsorbed cyclopentene molecules are present along the directions parallel and perpendicular to the the dimer row. These intermolecular interactions prevent adsorption on neighboring dimers along the dimer row direction which results in inhomogeneity of the C(001) surface. It also contributes to an increase of the energy barrier at the later stages of cyclopentene adsorption, thereby contributing to the low sticking coefficient. It is likely that this inhomogeneous adsorption structure of cyclopentene produces the broad C−H vibration spectra observed in the FTIR data.[6] In addition, partial H dissociation results in further stabilization over the molecular adsorption. However, the calculated reaction path for the H dissociation predicts an energy barrier of 1.27 eV, indicating that this will occur only well above room temperature.

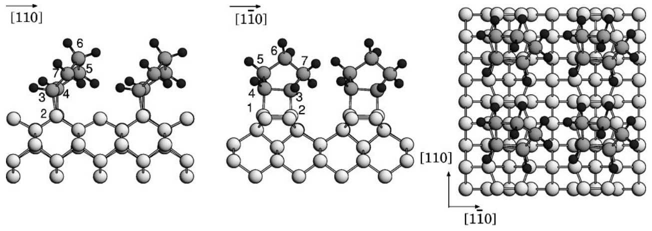

FIG. 1. Optimized geometry of the molecular adsorption of cyclopentene on C(001): the $p(2\times2)$ structure. Two different side views and the top view are displayed. The large and small circles represent C and H atoms, respectively. For distinction the C atoms in cyclopentene molecules are represented in darker gray.

TABLE I. Calculated adsorption energy of cyclopentene on C(001) for the molecular and the dissociative (D) adsorption with various coverages. For comparison our previous results on Si(001) (Ref. 9) are also given. The values in parentheses represent the results obtained from calculations with a 12 atomic-layer thickness of C(001) and $N_k=16$ in the (2×2) unit cell.

	Unit cell	θ (ML)	E_{ads} (eV)
C(001)	$p(2\times1)$	1	unstable
C(001)	$p(2\times2)$	0.5	2.04 (2.00)
C(001)	$p(2\times3)$	1/3	2.10
C(001)	$p(2\times4)$	0.25	2.12
C(001)	$p(4\times2)$	0.25	3.07
C(001)	$c(4\times2)$	0.5	2.90
C(001)D	$p(2\times2)$	0.5	3.69 (3.64)
C(001)D	$p(4\times2)$	0.25	5.12
C(001)D	$c(4\times2)$	0.5	4.68
Si(001)	$p(2\times2)$	0.5	1.60
Si(001)	$p(2\times1)$	1	1.17

II. CALCULATIONAL METHOD

The total-energy and force calculations were carried out using density-functional theory[14] within the generalized-gradient approximation.[15] The C and H atoms are described by ultrasoft[16] and factorized[17] norm-conserving pseudopotentials, respectively. A periodic slab geometry was employed with eight atomic layers and adsorbed cyclopentene molecules on both sides of the slab. The vacuum spacing 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 eight, four, two, two, two, and one points in the surface Brillouin zone of the (2×1), (2×2), (2×3), (2×4), (4×2), and (4×3) unit cells, respectively. All atoms except the two central C planes were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr. Here, the two central planes were taken at their calculated bulk separations of $a/4=0.893$ Å. Additional calculations with a 12 atomic-layer thickness of C(001) and 16 **k** points in the (2×2) unit cell show that the absolute value of the adsorption energy changes by about 0.05 eV, but the energy difference between the molecular and the dissociative adsorption was hardly changed (see Table I). The total energy of the isolated molecule was calculated in a $10\times10\times15$-Å supercell.

III. RESULTS

The adsorption energy is given by

$$E_{\mathrm{ads}}=-[E_{\mathrm{tot}}(\mathrm{C_5H_8/diamond})-E_{\mathrm{tot}}(\mathrm{diamond})-nE_{\mathrm{tot}}(\mathrm{C_5H_8})]/n, \tag{1}$$

where n is the number of cyclopentene per unit cell. The $p(2\times1)$ structure ($\theta=1$ ML) was found to be unbound with a negative adsorption energy. We next determined the optimized structure when cyclopentene is adsorbed on every other molecule in each row of dimers. This is the $p(2\times2)$ structure displayed in Fig. 1. The calculated adsorption energy (E_{ads}) and structural parameters such as the bond lengths and the bond angles are given in Tables I and II, respectively. We obtained an adsorption energy of 2.04 eV for $p(2\times2)$. This value is larger than the corresponding one ($E_{\mathrm{ads}}=1.60$ eV) on Si dimers (see Table I). The larger adsorption energy on C(001) reflects that in the $[2+2]$ product the new C−C bonding is stronger than the C−Si bonding on Si(001). Thus, our results do not support the suggestion of Carbone[10] that the cyclopentene adsorption may not take place on C dimers. (Neither do they prove her wrong, since the barrier to adsorption could be prohibitively large.) In Fig. 1 the geometry of the adsorbed cyclopentene shows tilting from the [001] direction toward the [110] direction. This is accompanied by twisting about the [001] direction yielding a torsion angle between the $\mathrm{C_3-C_4}$ molecular bond and the $\mathrm{C_1-C_2}$ dimer bond of 8.9° (for numbers representing C atoms, see Fig. 1). The torsion angle decreases to 0.2° when adsorbed cyclopentene molecules are separated by an unreacted C dimer row within a $p(4\times2)$ unit cell ($\theta=0.25$ ML). Such separated molecules have an adsorption energy of 3.07 eV, which is greater than that for the $p(2\times2)$ structure by $\Delta E_{\mathrm{ads}}=1.03$ eV (see Table I). This result indicates that in $p(2\times2)$ a large repulsive interaction between adsorbed molecules is present along the $[1\bar{1}0]$ direction. In $p(2\times2)$ ($\theta=0.5$ ML) the bond lengths d_{23} and d_{14} are somewhat different, 1.56 and 1.61 Å, respectively, but in $p(4\times2)$ these two bond lengths become 1.58 and 1.59 Å as a consequence of the reduction of the intermolecular interaction.

TABLE II. Calculated bond lengths (angstroms) and bond angles (degrees) of adsorbed cyclopentene molecules on C(001) within the molecular and dissociative (D) models. $\alpha_{1-2-3-4}$ represents the torsion angle between the $\mathrm{C_1-C_2}$ dimer bond and the $\mathrm{C_3-C_4}$ bond.

	θ (ML)	d_{12}	d_{23}	d_{34}	d_{41}	ϕ_{1-2-3}	ϕ_{2-3-4}	ϕ_{3-4-1}	ϕ_{4-1-2}	ϕ_{1-4-5}	ϕ_{2-3-7}	$\alpha_{1-2-3-4}$
$p(2\times2)$	0.5	1.61	1.56	1.55	1.61	88.8	92.4	89.3	88.2	125.1	122.8	8.9
$p(4\times2)$	0.25	1.61	1.58	1.56	1.59	89.6	90.9	91.0	88.6	124.7	123.6	0.2
$c(4\times2)$	0.5	1.62	1.56	1.56	1.58	89.5	91.0	91.1	88.3	125.3	123.6	0.4
$p(2\times2)$D	0.5	1.67	1.53	1.34	1.53	83.9	95.8	96.3	83.8	152.3	153.3	3.3
$p(4\times2)$D	0.25	1.66	1.53	1.35	1.53	84.2	95.7	95.8	84.2	150.1	150.3	1.8
$c(4\times2)$D	0.5	1.66	1.54	1.35	1.53	84.1	95.8	95.7	84.3	151.2	151.2	2.2

In order to examine steric interactions between adsorbed cyclopentene molecules along the [110] dimer row direction we considered $p(2\times3)$ and $p(2\times4)$ structures corresponding to $\theta=1/3$ and 0.25 ML. The calculated adsorption energies for $p(2\times3)$ and $p(2\times4)$ are 2.10 and 2.12 eV, respectively. Noting that $E_{\mathrm{ads}}=2.04$ eV for $p(2\times2)$ and that $p(2\times1)$ is unbound we can say that there is a very strong repulsive interaction between cyclopentene molecules on neighboring sites but with one or more empty dimers between the cyclopentenes the interaction remains repulsive but becomes very weak. Observation of Fig. 1 should convince the reader that there is no room to place additional cyclopentenes on the empty dimers in the $p(2\times2)$ structure. The saturation of more than half of the C dimers with cyclopentene is not allowed, contrasting with previous experimental[3] and theoretical[9] results for Si(001) whose larger lattice constant allows adsorption on every dimer. Our calculated 1.17- and 1.60-eV adsorption energies for the $p(2\times1)$ and $p(2\times2)$ structures on Si indicate a large repulsion between nearest-neighbor cyclopentenes (though not nearly as large as on diamond). This is consistent with the observed rapid adsorption of half a monolayer and the much slower adsorption rate thereafter, until nearly a full monolayer of cyclopentene is adsorbed on Si(001).

The large increase in bonding energy per adsorbed molecule on going from the $p(2\times2)$ to the $p(4\times2)$ structure led us to consider the possibility that a $c(4\times2)$ structure might reduce the repulsion between the cyclopentenes while maintaining the $\theta=0.5$-ML coverage of $p(2\times2)$. This turned out to be the case. The adsorption energy (Table I) of 2.90 eV for the $c(4\times2)$ is only 0.17-eV below that of the $p(4\times2)$ and with twice as many molecules adsorbed, $c(4\times2)$ is easily the ground state for undissociated cyclopentene on diamond (001). This is somewhat similar to the $c(2\times2)$ "dimerized zigzag" $\theta=1$-ML ground state we previously[9] determined for Si(001). In that case, unlike this, the dimers themselves were in a zigzag pattern. The clean Si(001) surface contains dimer rows. The breaking of dimer bonds required to turn the dimer rows into the zigzag pattern presents too large an energy barrier and STM data[3] proves that the zigzag ground state is not obtained. Unfortunately, there is no STM data for diamond, so we can only speculate. Our calculations indicate that if the $p(4\times2)$ structure could be obtained, then with further exposure the $c(4\times2)$ structure would be obtained with only a slightly greater energy barrier than for the $p(4\times2)$. However, the initial bonding will be on random sites with the only condition being that no nearest-neighbor dimers are occupied. Once adsorbed, the cyclopentenes will not diffuse, and therefore a fairly disordered surface will be obtained. Wherever there are cyclopentenes forming a (4×2) cell, one would expect an additional cyclopentene to be adsorbed at the cell center. This is unlike Si(001) where STM shows that over large regions of the surface, every dimer site is occupied and this accounts for the C$-$H vibration spectrum on the Si surface being much sharper than that on the diamond surface. In Fig. 2 the geometry of cyclopentene adsorbed in the $c(4\times2)$ structure is displayed. Again the molecules are tilted away from the [001] direction toward the [110] direction but the torsion angle between the C_1-C_2 dimer bond and the C_3-C_4 molecular bond is only 0.4° which is another indication that the intermolecular forces are much weaker than in the $p(2\times2)$ structure and only very slightly stronger than in the $p(4\times2)$. See Table II for a comparison of all bond lengths and angles.

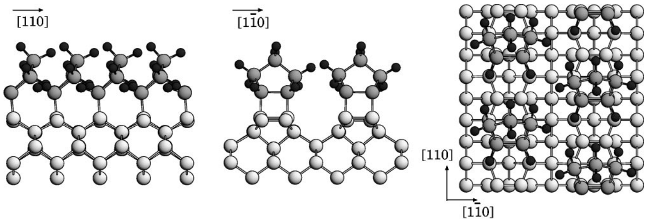

FIG. 2. Optimized geometry of the molecular adsorption of cyclopentene on C(001): the $c(4\times2)$ structure. Two different side views and the top view are displayed.

For Si we studied the dissociative state where the hydrogens on carbon atoms 3 and 4 in Fig. 1 rebonded to the Si dimer.[18] There was an energy cost of 0.09 eV in the (2×1) case and 0.57 eV in the (2×2) case but an energy gain of 0.01 eV when only every other cyclopentene was dissociated in the (2×1) case. From this we see that there are two contributions to the dissociation energy. There is a net energy cost to break the H$-$C bonds, break a Si dimer bond, and form the H$-$Si bonds. But there is an energy gain in the (2×1) case due to reduced repulsion between the cyclopentenes when those two hydrogens are removed. For diamond the situation is considerably different. The lowest energy will be obtained if the hydrogens bond to the unoccupied dimers because it is much easier to break their π bonds than it is to break the σ bonds of those dimers whose π bonds have been used to bond the cyclopentene. From Tables I and II we find that dissociation results in energy gains of 1.65, 2.05, and 1.78 eV and torsion angles of 3.3°, 1.8°, and 2.2° for the $p(2\times2)$, $p(4\times2)$, and $c(4\times2)$ cases, respectively. The C pentagon does, however, regain its planar structure (see Fig. 3). From this we conclude that there is intrarow repulsion between the dissociated hydrogens and the C_5H_6 molecules in all three cases as well as interrow repulsion between hydrogens in the $p(2\times2)$ case and slightly less interrow repulsion between H and C_5H_6 in the

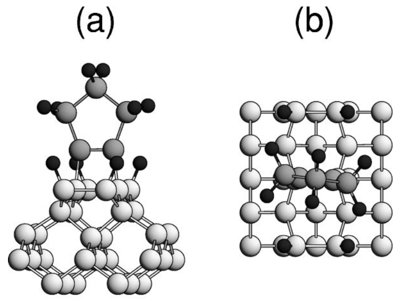

FIG. 3. Optimized geometry of the dissociative adsorption of cyclopentene on C(001): (a) the side view and (b) the top view of the $p(2\times2)$ structure. Here the side view is rotated about the (001) axis by 9°, away from the [1$\bar{1}$0] direction.

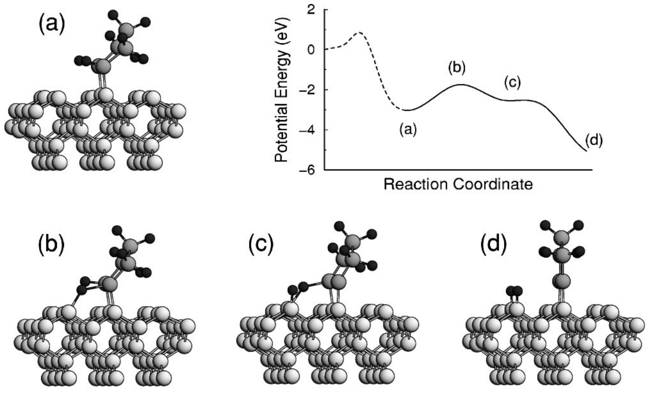

FIG. 4. Calculated energy profile of adsorbed cyclopentene molecule on C(001). The atomic geometries at four representative points are given: (a) the molecular adsorption, (b) and (c) the transition states, and (d) the dissociative adsorption. The dashed line in the energy profile represents an assumed reaction barrier for the [2+2] cycloaddition. Here the side view is rotated about the (001) axis by 9°, away from the $[1\bar{1}0]$ direction.

$c(4\times2)$ case. Note that the C_3-C_4 bond length is shortened to ~1.34 Å because upon dissociation of the hydrogens, it becomes a double bond.

To study the reaction path for the above-mentioned H dissociation, we calculate the energy profile of the optimized structures by increasing the distance between the dissociated hydrogen and its bonded C atom while allowing all other atoms to relax to their equilibrium positions.[19] In Fig. 4 the calculated energy profile and the atomic geometries of several adsorption states are displayed. The dashed line represents an assumed energy barrier to adsorption which results in the small sticking coefficient. Here, we use a large unit cell of $p(4\times3)$ to make negligible the intermolecular interactions. We find that after one of the two H atoms bonded to C_3 and C_4 transfers to a neighboring dimer, the other H atom transfers with either no barrier or one so small that we could not detect it. The energy barrier for the dissociation of the first H atom is obtained to be about 1.27 eV. Using an Arrhenius-type activation process with a typical value[20] ($\sim10^{14}$ Hz) for the preexponential factor the reaction rate at room temperature is estimated as $\sim5\times10^{-8}$ s^{-1}, indicating no thermal activation at room temperature. Thus, we can say that the dissociative adsorption of Fig. 3 is kinetically prohibited because of the existence of a high activation barrier, though it is thermodynamically more stable than simple molecular adsorption. This is consistent with the FTIR data[6] which show no evidence for H dissociation.

IV. CONCLUSIONS

Our density-functional theory calculations for the adsorption of cyclopentene on C(001) support the [2+2] cycloaddition reaction on C dimers. Although our calculations cannot disprove the assertion[10] that adsorption occurs only on defects we believe experiment[6,13] does disprove it. Although experiment[6,13] was interpreted to yield near monolayer coverage, both the dissociated and undissociated ground states are the $\theta=0.5$-ML $c(4\times2)$. The repulsion between the cyclopentenes causes at least some disorder which is experimentally[6] observed, and must cause the coverage to be somewhat less than 0.5 ML.

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[18] When $\theta=0.5$ ML the hydrogens could bond to dimers either with or without adsorbed cyclopentenes. To compare with $\theta=1$ ML we had them bond to the former.

[19] In order to determine the reaction path and hence the coordinates

of the transition states in Figs. 4(b) and 4(c), we used the gradient projection method where the distance between the dissociated hydrogen and its bonded C atom (but not the angle of that bond) is constrained; see D. A. Wismer and R. Chattery, *Introduction to Nonlinear Optimization* (North-Holland, Amsterdam, 1978), pp. 174–178.

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