

Coverage dependence of the 1-propanol adsorption on the Si(001) surface and fragmentation dynamics

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The geometric, electronic, energetic, and dynamic properties of 1-propanol adsorbed on the Si(001)-(2×1) surface are studied from first principles by use of a slab approach. The 1-propanol molecule initially interacts with the Si surface through formation of a dative bond; subsequently the physisorbed 1-propanol molecule reacts with the surface by cleavage of the O-H bond, and the Si(001)-(2×1) surface undergoes further reconstruction as a result of the adsorption of the organic species. The band structure and density of states are first analyzed for this system. The band gap of the Si/1-propanol film increases as the coverage level is enhanced. Good agreement is found with available experimental data.

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I. INTRODUCTION

The chemisorption of organic molecules on silicon surfaces is a highly topical subject of current research, both experimental and computational. This interest may be ascribed to both the fundamental nature of this problem, involving the interaction between finite units and periodic substrates, and also its relevance to various areas of recent technology, such as insulator films, nanolithography, chemical and biological sensors, and molecular electronics. The organic layers are formed by depositing organic compounds on the semiconductor surface. In order to optimize this process, the understanding of the interaction between the surface and the organic species is crucial. The majority of the reactions between the semiconductor surface and organic molecules occur at or near the dangling bonds of the reconstructed surface. For a silicon (001) surface, the 2×1 reconstruction leads to the formation of silicon dimers, where a strong σ bond and a weak π bond between the two dimer atoms is observed.¹ It is well known that for hydrocarbons, the C-C double bonds break the dimer π bond and lead to the formation of new surface bonds that are energetically favorable.² Employing a similar mechanism, one can produce well-ordered organic films/Si structures with a stable and uniform interface. These composites of silicon surfaces coated by organic films may lead to novel types of micro-electronic devices that exploit the rich variety of functional groups of the organic species.

In the past decade, the reaction between the silicon surface dimers and alcohols have attracted much attention.³⁻¹¹ For instance, the adsorption of ethanol on Si(001) was first observed by using surface infrared absorption spectroscopy.⁴ At room temperature, the ethanol is adsorbed dissociatively to form surface bond hydrogen and ethoxy groups, as a consequence of O-H bond breaking. The adsorption of ethanol on Si(001) at room temperature has also been studied employing high-resolution synchrotron radiation photo-

emission.⁵ In this case, O-H bond scission occurs. This behavior is at variance with ethanol adsorption on Si(111)-(7×7),⁶ where the C-O bonds were found to be broken. The reaction of 1-propanol (C₃H₈O) with the Si(001)-(2×1) surface was investigated in the pioneering work of Zhang *et al.*¹¹ by Auger electron spectroscopy and thermal desorption spectroscopy. From this study, the 1-propanol molecule initially interacts with the Si surface through the formation of a “dative bond,” followed by further reaction of the physisorbed 1-propanol molecule with the surface by O-H bond cleavage. From the work reported in Ref. 11 the O-H bond cleavage is a kinetically favored reaction, but the O-C bond cleavage is thermodynamically preferred.

So far, there is no full first-principles theoretical calculation that provides a complete description of the 1-propanol molecule reaction with the Si(001) surface, excepting a preliminary calculation in the framework of a single-dimer cluster model for the Si(001) surface.¹¹ Adopting the latter model, however, the surface-specific aspects of the problem at hand cannot be treated adequately. Thus, it is impossible to simulate the “buckling” of the surface dimer. As mentioned in the work of Zhang *et al.*,¹¹ the results based on a single-dimer model should be substantially improved by considering an array of dimer clusters to account adequately for charge delocalization or surface relaxation phenomena. Secondly, the electronic properties, such as the band structure and the density of states (DOS) distribution for this system, have not been discussed before. For in-depth analysis of the substrate-adsorbate interaction, however, the understanding of these features is of crucial importance. Thirdly, studying the dependence of various characteristic properties on the 1-propanol coverage is hardly feasible in the framework of a single-dimer model.¹² Finally, the mechanism of the reaction between the 1-propanol molecule and the Si(001) surface has not been studied before. Such a simulation, involving the interaction of the finite molecular adsorbate and the periodic substrate at room temperature has been performed in the con-

text of the present work by means of *ab initio* molecular dynamics (MD), as described in further detail below.

Guided by this motivation, in the present contribution we study the adsorption of 1-propanol on the Si(001)-(2×1) surface by use of the VASP code,¹³ involving a slab geometry and periodic boundary conditions. The introduced model allows for an appropriate description of the Si(001) surface with and without the adsorption of the 1-propanol molecule as the reconstruction of the Si surface before and after adsorption can be displayed manifestly. Section III of this contribution contains a detailed analysis of the most prominent reactions undergone by 1-propanol on the Si(001) surface, including the calculations of the reaction barriers corresponding to various reaction pathways. Further, the charge density in a plane including the 1-propanol oxygen and a surface silicon atom, the surface band structure within the silicon fundamental gap, and the DOS and partial DOS distributions projected on the substrate atoms as well as the 1-propanol molecule or its fragments are discussed. In addition, we outline the variation of the binding energies, the energy barriers, the DOS, and the energy gap with the degree of coverage, where four coverage levels [0.125, 0.25, 0.5, and 1.0 (ML)] are taken into account. Finally, we will make allowance for finite temperature and compare the characteristic reaction mechanisms at $T=300$ K with those found at $T=0$ K.

II. COMPUTATIONAL METHOD

Our calculations were carried out by use of the VASP code.¹³ Density functional theory (DFT) was applied on the level of the generalized gradient approximation¹⁴ (GGA) in conjunction with the projector augmented wave (PAW) pseudopotential.^{15,16} The wave functions are expanded in a plane wave basis with an energy cutoff of 400 eV, whereas the cutoff for the augmentation charges is 645 eV. The Brillouin zone integrations are performed by use of the Monkhorst-Pack scheme¹⁷ with the origin shifted to the Γ point. We utilized a $3 \times 3 \times 1$ k point mesh for the geometry optimization, and an $8 \times 8 \times 1$ k point mesh for the DOS calculation. The Si(001)-(2×1) surface is modeled adopting a supercell geometry with an atomic slab of five Si layers where terminating hydrogen atoms passivate the Si atoms. The supercell consists of a 4×4 ideal cell, i.e., 80 atoms and 32 H atoms. The Si atoms in the top four atomic layers are allowed to relax, while the Si atoms in the bottom layer and the adjacent passivating H atoms are fixed to simulate bulk-like termination.^{18–20} The vacuum region is about 19 atomic layers, which exceeds the length of the 1-propanol molecule and provides sufficient spacing for the present MD simulation. We performed computations on the pure substrate that were intended to examine the accuracy of our approach. Thus, we increased the energy cutoff to 500 eV and the number of k points to $8 \times 8 \times 1$. Neither of these tests led to any appreciable changes of total surface energy; in both cases, the difference amounted to less than 1.2%. The energy barriers characterizing different reaction paths were calculated by the “climbing” nudged elastic band^{21–23} method with six images, which permits identifying minimum energy paths in

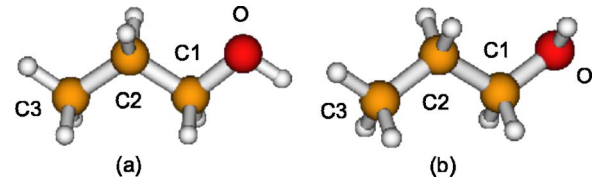


FIG. 1. (Color online) 1-propanol molecule structures in the gas phase.

complex chemical reactions. *Ab initio* MD simulations were performed by use of a Verlet algorithm to integrate Newton’s equations of motion. The canonical ensemble was simulated using the Nosé algorithm.²⁴

As a test, we calculated the structural properties of the free 1-propanol molecule, and found the obtained bond lengths to be in good agreement with the literature values.^{25,26} The deviation from these earlier results was found to be less than 3%. The structures of the isolated 1-propanol molecule are shown in Fig. 1. Further, the calculated 1-propanol ionization energy is within 8% of the experimental value, 10.18 ± 0.06 eV.²⁷

The calculated geometrical parameters are given in Table I, where the unit of the bond length is angstroms.

It should be noted that there are actually five conformers for the 1-propanol molecule which differ from each other with respect to the dihedral angles. The isomers (a) and (b) as shown in Fig. 1 are the energetically favored species,²⁸ and these two conformers are readily interchanged at room temperature, since the OH torsion barriers are quite low. Our calculations involve the structure (a) which deviates from structure (b) by a difference in binding energy lower than 0.01 eV.

We further computed energetic and geometric parameters pertaining to the 2×1 reconstruction of the bare Si(001) surface (its explicit illustration can be found from Fig. 1 in Ref. 29). The 2×1 reconstructed silicon surface is displayed in Fig. 2. Figure 2(a) reveals the three silicon top layers, and Fig. 2(b) illustrates the buckling angle, which is defined as the angle between the dimer row and the horizontal plane. The Si dimers are oriented along the x axis or $[110]$ direction, and the dimer rows are along the y axis or the $[\bar{1}10]$ direction.

For the 2×1 surface reconstruction with asymmetric Si dimers, the energy gain is 1.6 eV per dimer. The internuclear

TABLE I. The calculated structural parameters of the isolated two isomers of the 1-propanol molecule.

	Structure (a)	Structure (b)
$d(\text{O-H})$	0.97	0.97
$d(\text{O-C1})$	1.44	1.43
$d(\text{C1-C2})$	1.52	1.52
$d(\text{C2-C3})$	1.53	1.53
$\angle \text{H-O-C1}$	108.5	108.0
$\angle \text{O-C1-C2}$	108.3	113.5
$\angle \text{C1-C2-C3}$	112.7	112.7
Dihe(H-O-C1-C2)	179.9	61.3

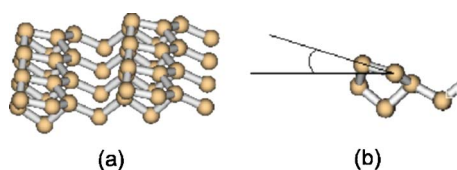


FIG. 2. (Color online) The 2×1 reconstructed silicon surface. The three top layers are shown.

distance between the two Si centers is 2.32 Å. The distance between two adjacent dimers perpendicular to the row is 3.86 Å. The distance between the “up” Si atom of one dimer and the “down” Si atom of the next is 5.57 Å. The buckling angle is 18°. These results agree with existing experimental³⁰ data and other calculations.¹⁸

III. RESULTS AND DISCUSSION

A. The physisorbed and chemisorbed configurations

In this section, we first describe the stable physisorbed configurations of the 1-propanol molecule on the Si(001)-(2×1) surface for 0.125 ML, where three nondissociative structures are identified. Subsequently, we consider seven dissociated structures which correspond to chemisorbed configurations. From these seven cases of chemisorption, we select the two most stable ones. Further, we characterize the modification of the bare Si(001)-(2×1) reconstructed surface due to the physisorbed and chemisorbed 1-propanol molecules. Moreover, in an effort to examine which one among the chemisorbed structures is most likely to be observed experimentally, we calculate the energy barriers relevant to the chemisorbed configurations. The charge density in the plane passing through the oxygen and silicon atom is drawn to show how the O-Si bond is formed. The surface band structures, the electronic DOS and partial DOS projected on the Si atoms and the 1-propanol molecule (or its fragments) are obtained to characterize the interaction between the substrate and the adsorbate.

Here we only focus on the adsorbed structures obtained by an exothermic process, i.e., the composite of the surface and the adsorbed species is lower in energy than the free 1-propanol molecule and the bare Si(001)-(2×1) surface in separation from each other. Experimentally, it has been demonstrated that the 1-propanol molecule and its fragments are oriented vertically with respect to the surface.¹¹ This adsorption geometry is therefore adopted for our treatment of the physisorbed and chemisorbed configurations.

Our calculated results confirm that the 1-propanol molecule initially interacts with the Si(001)-(2×1) surface via the formation of a “dative bond” between the oxygen atom and the electrophilic “down” Si atom of the surface dimer. Specifically, the O-Si bond may be characterized as a covalent connection arising from the lone pair of the O atom. The 1-propanol molecule remains essentially intact (this motivates our nomenclature I-1, I-2, and I-3 for the physisorbed configurations) or undissociated on the physisorbed sites, and assumes various orientations of the O-H bond with respect to the Si surface. The obtained structures are shown in

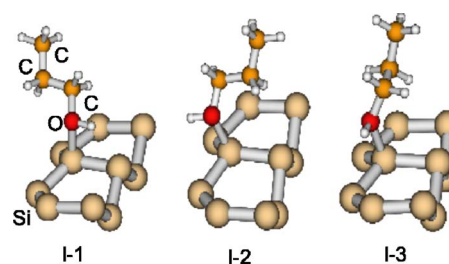


FIG. 3. (Color online) Three stable physisorbed configurations of the 1-propanol molecule on the Si(001) surface. The yellow (largest), red, orange, and white (smallest) spheres (from bottom to top) represent the silicon (Si), oxygen (O), carbon (C), and hydrogen (H) atoms, respectively. The atoms are distinguished by labels applied in the figure with subscript I-1. To illustrate the interaction between the 1-propanol molecule and the Si(001)-(2×1) surface, we display only a few surface Si atoms. Our simulation includes 16 Si atoms in each layer.

Fig. 3 which illustrates that the direction of the O-H bond can be parallel (I-1), antiparallel (I-2), or perpendicular (I-3) to the Si dimer. However, the energies of the three configurations are very close to each other, i.e., the rotation of the 1-propanol molecule around the Si-O bond is quite facile.

In the single-dimer cluster calculation, only the physisorbed structure similar to I-2 was considered,¹¹ while we include three possible physisorbed configurations I-1, I-2, and I-3 here. Table II shows that the reported binding energy¹¹ (0.39 eV) is considerably smaller than that found in this work (0.72 eV). This discrepancy might be attributed to the difference between the single-dimer model and the periodic approach followed in the present approach.

For the bare Si(001)-(2×1) surface, the buckling angle with the horizontal plane is 18.0°. As a consequence of 1-propanol physisorption, the buckling angles for I-1, I-2, and I-3 become 8.7°, 11.0°, and 10.8°, respectively. For the adjacent Si dimer, the corresponding buckling angles are 17.9°, 17.8°, and 17.0°. As the latter values are close to the angle found for the bare Si(001) surface, 18.0°, the interaction between the 1-propanol molecule and the adjacent Si dimer is quite weak.

We have verified that the physisorption in the case I-1, I-2, or I-3 is a barrierless reaction, which starts from a 1-propanol molecule far from the surface. Once this is physisorbed and attached to the surface by a “dative bond,” the 1-propanol can proceed to react with the surface via a number of pathways, which break one or more molecular bonds to form dissociated configurations of increased stability. The eight principal dissociated structures arising from H atom loss or O-C bond cleavage are shown in Fig. 4.

The F-1 structure is obtained by breaking the O-H bond and detaching the H atom until it attaches to the “up” Si atom of the same dimer to form a new H-Si bond. This configuration has the second largest binding energy (2.59 eV). The remaining alkoxy fragment is bonded to a Si surface dimer atom, while the separated H atom forms a bond with the other Si atom of the same dimer. The binding energy decreases as the H atom is attached to a Si atom of an adjacent dimer. For the ethanol molecule, the axis of the

TABLE II. The binding energies in eV per 1-propanol molecule and structural parameters of the configurations shown in Figs. 3 and 4. The data are for 0.125 ML coverage. In parentheses, the binding energy values obtained by a single-dimer model are indicated.

	I-1	I-2	I-3	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8
E_{bind}	0.75	0.72	0.68	2.59	2.89	1.54	1.66	1.66	1.65	2.22	2.46
		(0.39)		(2.62)	(3.22)	(1.66)	(1.71)	(1.71)			
$d(\text{O-H})$	1.01	0.98	0.98		0.97	0.98	0.99	0.97			
$d(\text{C1-O})$	1.48	1.49	1.49	1.44		1.44	1.43	1.43	1.28		
$d(\text{C1-C2})$	1.51	1.51	1.51	1.52	1.53	1.53	1.52	1.52	1.49	1.53	1.53
$d(\text{C1-C3})$	1.53	1.53	1.53	1.53	1.54	1.53	1.53	1.53	1.53	1.54	1.53
$d(\text{O-Si})$	1.96	1.95	1.99	1.66	1.68				1.79	1.57	1.57
$d(\text{C-Si})$					1.93	1.95	1.94	1.91		1.91	1.91
$d(\text{H-Si})$				1.50		1.50	1.50	1.50	1.50	1.50	1.50
$d(\text{Si-Si})$	2.39	2.38	2.40	2.43	2.44	2.41	2.41	2.43	2.41	2.46	2.44
Buckling (degree)	8.7	11.0	10.8	1.9	4.1	4.5	5.7	1.6	2.7	1.3	1.9

methyl group is almost perpendicular to the Si(001) surface,⁴ but in the case of 1-propanol, the corresponding axis includes an angle of about 75° with the surface. Since the considered coverage of 0.125 ML is sparse, the repulsion between the adjacent 1-propanol molecules is negligible. Thus we conclude that the vertical orientation of the 1-propanol molecule is not the result of the repulsion between alkoxy groups, which is consistent with the cases of ethanol adsorption.⁴ We have seen that the O atom forms a single polar covalent bond with only one Si atom of the surface dimer, which reflects the localized and directed nature of the Si dangling bond.

The F-2 configuration is described by C1-O bond cleavage. The OH group and the alkyl fragment are bonded to the same Si dimer. If these two fragments are attached to adjacent dimers, the binding energy decreases. As Table II shows, the F-2 configuration is thermodynamically most stable, i.e., it has the largest binding energy (2.89 eV).

The F-3, F-4, and F-5 configurations are characterized by breaking the C1-H, C2-H, and C3-H bonds, respectively, where the C1 (or C2, C3) atom is bonded to a Si atom and

the detached H atom forms a new bond with the other Si atom of the same dimer. From the respective binding energy one finds that the configuration of the C-H cleavage is of lesser stability than both F-1 and F-2.

To examine whether the F-1 and F-2 structures undergo further bond rupture, we consider the configurations F-6, F-7, and F-8. F-6 is described by the cleavage of a C-H bond in F-1, and the H atom is attached to the adjacent dimer. The energy of F-6 is higher than that of F-1 by 0.9 eV. F-7 and F-8 are obtained from F-2 by further dissociating the O-H bond and attaching the corresponding H atom to the down and up Si atoms of the adjacent dimer. These structures are energetically less favored than the original F-2 configuration.

In going from I-1 to F-1 (the H atom binding with the up Si atom), a substantial increase in the binding energy is observed. The comparable transition from F-2 to F-7, however, is associated with a large decrease in the binding energy. This difference is related to the fact that I-1 is a physisorbed structure, while F-1 is a chemisorbed one, making plausible its higher stability as compared with I-1. Chemisorption is realized for the configuration F-2, involving saturated covalent bonding of the oxygen atom which forms one bond with the down silicon atom and another one with the hydrogen atom. For the F-7 configuration, in contrast, the hydrogen atom is detached from the oxygen atom which consequently is unsaturated, implying a decreased binding energy for the F-7 structure. It may be assumed that oxygen in this configuration forms a double bond with the down silicon atom. The latter, however, already forms two bonds with next layer silicon atoms, and a third one with its silicon dimer partner atom, which leaves a single bond between oxygen and silicon as the only possibility. From an energetic point of view, F-1 and F-2 are most stable, corresponding to the tendency of 1-propanol to break the C-O bond or the O-H bond. Therefore, the subsequent discussion will be limited to the configurations F-1 and F-2.

To see that increasing the plane wave basis (or the energy cutoff) has only a slight effect on the above adsorption energies, we have calculated the adsorption energies for the I-1, I-2, F-1, and F-2 configurations at 500 eV. If the energy cutoff is 400 eV, the adsorption energies for the same con-

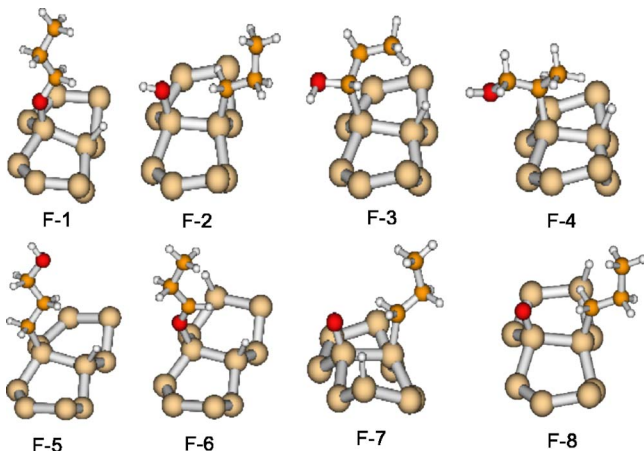


FIG. 4. (Color online) The fragmented chemisorption structures of 1-propanol on the Si(001) surface. For the sake of clarity, we have included only ten Si atoms in this illustration.

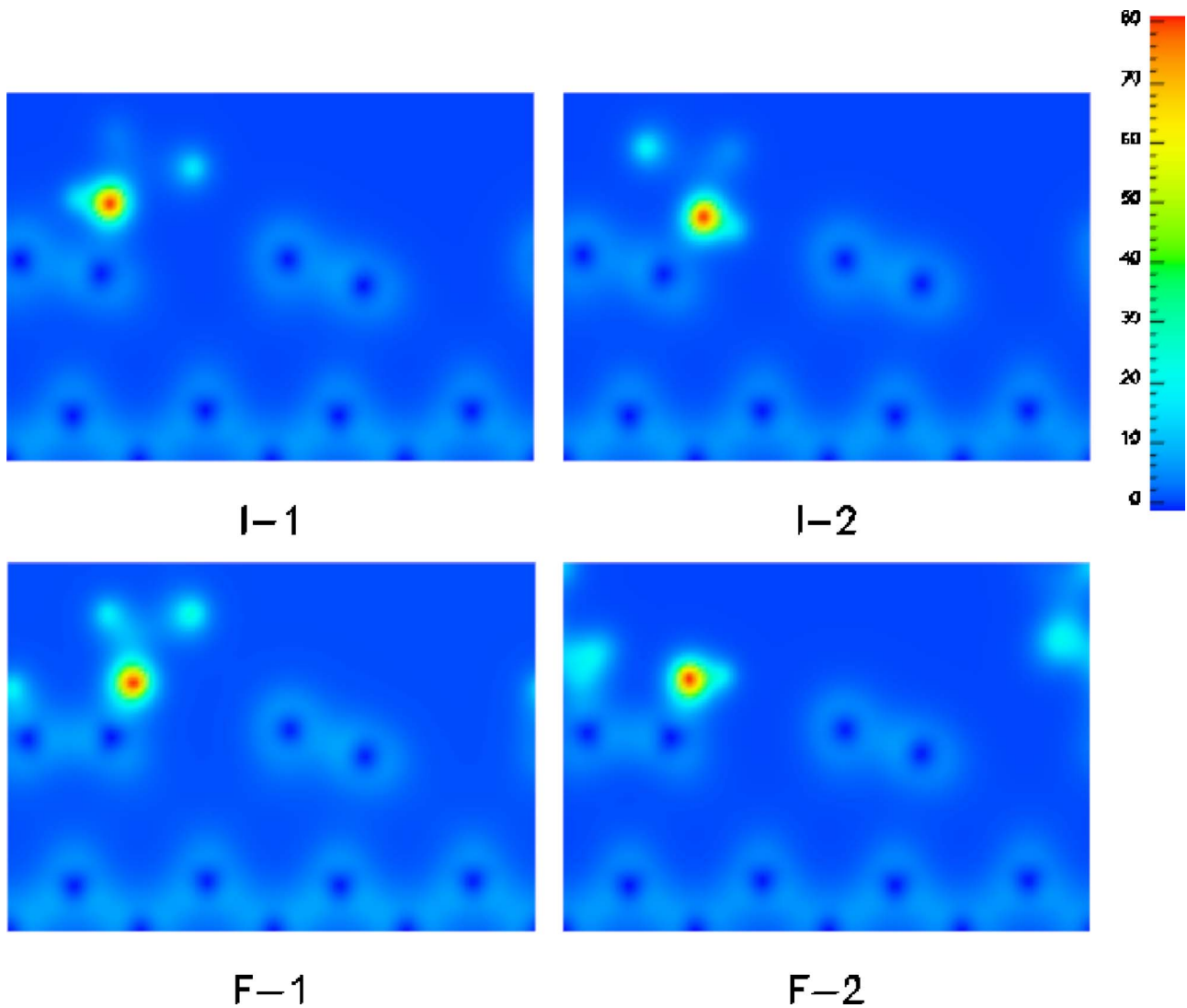


FIG. 5. (Color online) The charge density in the plane extended in the directions $[110]$ and $[\bar{1}10]$ for the configurations I-1, I-2, F-1, and F-2. The unit for the charge density is $0.01 e/\text{\AA}^3$. The red zone (brightest) is due to the higher charge density of the oxygen atom, the blue spots (darkest) correspond to the silicon charge density. The charge density between the O and Si atoms shows the polar O-Si bond.

figurations are 0.75, 0.72, 2.59, and 2.89 eV, respectively. When the energy cutoff is 500 eV, the corresponding energies are 0.75, 0.71, 2.56, and 2.91 eV. The difference between the two sets of results amounts to less than 1.2%.

The charge density in the plane passing through the oxygen and the silicon atom (extended in the directions $[110]$ and $[\bar{1}10]$) is shown in Fig. 5. It is calculated within the pseudopotential framework. The analysis of the charge density clearly shows that a polar dative bond for the physisorbed structures I-1 and I-2 (O-Si bond lengths for them are 1.96 and 1.95 \AA) and the polar covalent bond for chemisorbed structures F-1 and F-2 (O-Si bond lengths for them are 1.66 and 1.68 \AA) have been formed.

B. Energy barriers

To assess which chemisorbed structure is most likely to be observed experimentally, we have calculated the energy barriers relevant to the chemisorbed configurations. Table III

shows the energy barriers for the respective reactions. For the physisorbed structures I-1, I-2 and I-3, the reaction proceeds without barrier. For the cases of chemisorption, we have calculated the energy barriers for the processes that lead from I-1 to F-1, I-2 to F-2, and F-1 to F-6, respectively. The energy barriers have been calculated by the climbing nudged

TABLE III. The energy barriers E_b and transition state energy levels E_{TS} with respect to the energy of the 1-propanol molecule and the Si(001) surface in separation from each other.

Reaction	E_b (eV)	E_{TS} (eV)
1-propanol+Si(001) \rightarrow I-1	0	
I-1 \rightarrow F-1 (O-H breaking)	0.05	-0.70
I-2 \rightarrow F-2 (O-C breaking)	1.34	0.62
F-1 \rightarrow F-6	2.9	0.31

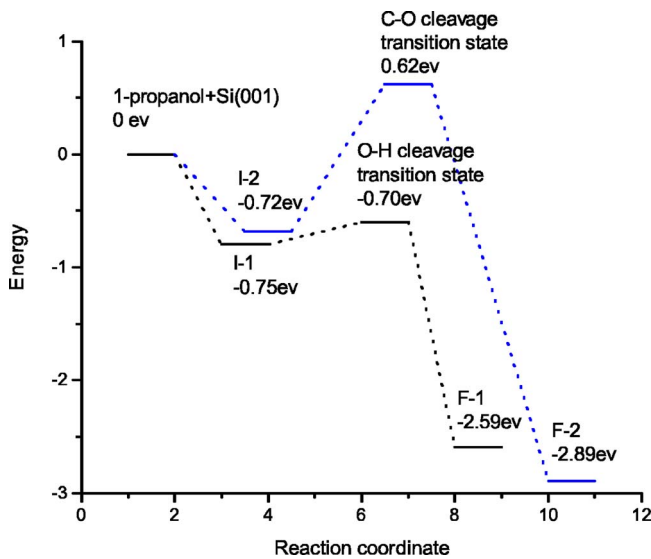


FIG. 6. (Color online) The relative energy levels along the O-C and O-H cleavage reaction paths.

elastic band method,^{21–23} where six equidistant images have been used.

For the transformation to the F-1 configuration, I-1 is the most favorable initial structure since its O-H bond is already oriented parallel to the Si dimer row. This reaction is a proton transfer process from oxygen to the electron-rich, nucleophilic “up” silicon atom of the dimer. The I-1 to F-1 reaction is characterized by an energy barrier of 0.05 eV. The binding energy of I-1 is 0.75 eV which implies that the barrier for the whole process, i.e., adsorption into the I-1 structure followed by transition to the F-1 structure, is below the initial energy, namely the of the free 1-propanol molecule and a bare Si(001) surface. Since the binding energy of F-1 is 2.59 eV, the I-1 \rightarrow F-1 process is exothermic.

From the physisorption case I-2 to configuration F-2, involving the breaking of a C-O bond, the energy barrier is 1.34 eV. The binding energy of I-2 is 0.72. Therefore, the transition state energy is higher than the reference energy of the free 1-propanol molecule and the bare Si(001) surface. The binding energy of F-2 is 2.89 eV, making the I-2 \rightarrow F-2 process exothermic too. Thus the O-C bond cleavage is thermodynamically stable, but the O-H bond cleavage is kinetically favored. In other words, the O-C bond cleavage has the highest binding energy, while the O-H bond cleavage has a smaller energy barrier than the O-C bond cleavage. This confirms, on the basis of a more adequate periodic model, the conclusion reached by Zhang *et al.*¹¹ in the framework of a finite cluster approach. The relative energies along the O-C and O-H cleavage reaction paths are schematically illustrated in Fig. 6.

Zhang *et al.*¹¹ suggested that the initial O-H bond cleavage might be followed by a hydrogen elimination reaction to result in aldehydes and hydrogen. Table III shows that the energy barrier for the transition from the O-H cleavage configuration F-1 to the configuration F-6 is relatively high. One concludes that the respective reaction is not preferred. Similarly, the transition from F-2 to F-7 configuration is not favored.

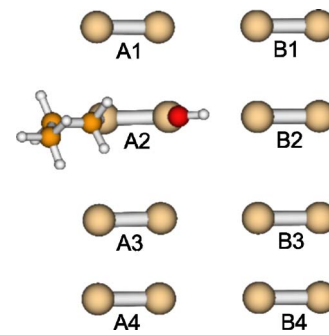


FIG. 7. (Color online) The labels and positions of eight dimer units in the top Si layer, where the horizontal direction is along $[110]$ and the vertical one is along $[\bar{1}10]$.

The undissociated structures I-1, I-2, and I-3 can be interpreted as metastable precursors for the more stable F-1 configuration. These precursors do not have sufficient binding energy at room temperature to compete as observable reaction products, i.e., the cleavage of H is too fast for any of the physisorbed structures to be observed. The MD simulation outlined below gives additional support to this interpretation.

C. Band structure

A sketch of the eight relevant Si dimer units in the top Si layer is shown in Fig. 7 for unambiguous reference, where the horizontal (vertical) corresponds to the $[110]$ ($[\bar{1}10]$) directions, respectively. For 0.125 ML, the 1-propanol molecule or its fragments are adsorbed to the A2 dimer.

The up Si atoms are located at the left dimer ends, the down Si atoms at the right. However, as described above, after the adsorption of the 1-propanol molecule to the down Si atom, the latter is raised, i.e., the buckling angle decreases.

The surface band structures within the fundamental band gap of the silicon for the configurations I-1, I-2, F-1, and F-2 for 0.125 ML, are depicted in Fig. 8. The k points Γ, J, K, J' are four vertices of the square of the quarter part of the surface Brillouin zone (the relative positions of Γ, J, K, J' points can be seen from Fig. 3 in the work of Ramstad *et al.*²⁹).

Figure 8 reveals that there are seven, nine, eight, and eight surface bands within the fundamental band gap of silicon for the I-1, I-2, F-1, and F-2 configuration, respectively. The remaining valence (conduction) bands lie in the lower (higher) shaded area. In the I-1 configuration, for the valence bands (occupied), the top one is labeled I-1-O1, and the next lower one is I-1-O2, etc. For the conduction band (unoccupied), the bottom one is referred to as I-1-U1, the higher ones are I-1-U2, I-1-U3, I-1-U4, and the highest one is I-1-U5. The same nomenclature is used for the surface bands of the other three configurations.

The two highest surface valence (O1 and O2) and the two lowest surface conduction bands (U1 and U2) contain the information about the adsorption and are thus sensitive to the structural features of the surface. The conduction bands U4 and U5, for instance, exhibit the same atomic orbital compo-

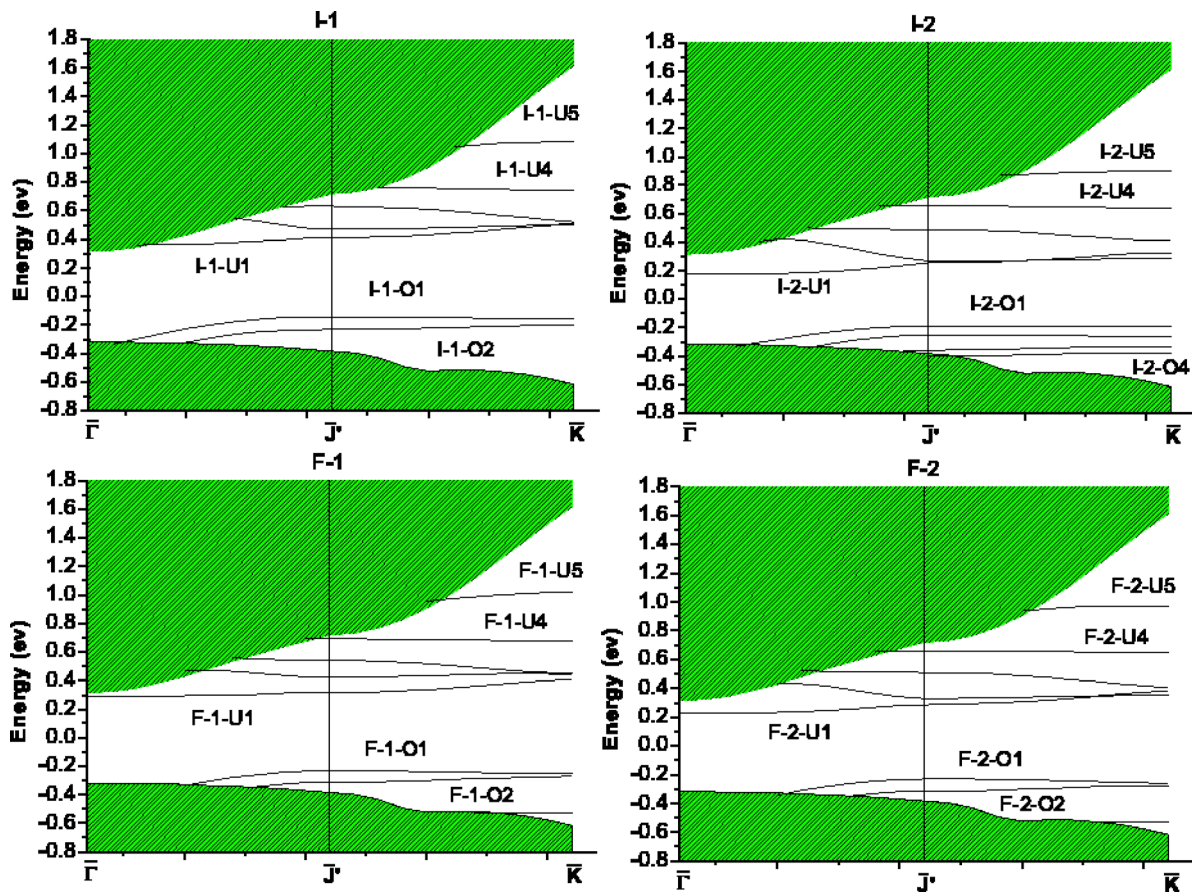


FIG. 8. (Color online) Surface band structures for the configurations I-1, I-2, F-1, and F-2 at 0.125 ML. The shaded areas represent the projected bulk band structure, while surface states are represented as solid lines.

sition for all four configurations I-1, I-2, F-1, and F-2. It is therefore sufficient to consider only the top two occupied valence bands (O1,O2) and bottom two unoccupied conduction bands (U1,U2), and the main contributions to these four bands are shown in Table IV for the configurations I-1, I-2, F-1, and F-2. Table IV indicates that the band I-1-O1 contains the information about the 1-propanol adsorption. The A1 and A3 contributions to the valence band I-1-O1 are an electronic fingerprint of the adjacent dimers, while the 1-propanol physisorption leaves their geometric structure unaffected, as reflected by their buckling angles.

Here we note that within the fundamental band gap of silicon, there is no conduction band for a Si-O bonding due to the adsorbate. In case of the acetonitrile adsorption on the silicon surface,¹⁹ in contrast, a conduction band with both Si and N contributions is found within this gap, which indicates that the acetonitrile electronic interaction with the silicon substrate might be stronger than that for 1-propanol.

D. Density of states

The electronic density of states as well as the partial DOS projected on Si atoms and the 1-propanol molecule (or its fragments) for the physisorbed configurations I-1 and I-2 and the chemisorbed configurations F-1 and F-2 are shown in Figs. 9 and 10. The top, middle, and bottom layers represent

the DOS of the total slab, the partial DOS projected on Si, and the 1-propanol molecule (or its fragments for chemisorbed structures), respectively. The partial DOS projected on the 1-propanol molecule (or its fragments) is much lower in magnitude than the DOS of the total slab for 0.125 ML coverage. To show its features manifestly, we have rescaled this distribution (vertical axis) (see Figs. 9 and 10), and the rescale factor is 10.

We consider the DOS with special emphasis on the peaks around the Fermi level and some characteristic peaks. The partial DOS projected on the Si atoms has almost the same profile as that of the DOS of the total slab, which indicates that, for 0.125 ML coverage, the total DOS is dominated by the Si(001) surface states.

In the following discussion, we focus on the two projected partial DOS distributions. The main components of the peaks of the partial DOS distributions projected on the Si atoms and 1-propanol (or its fragments) are indicated in Table V for the configurations I-1, I-2, F-1, and F-2.

Comparing the partial DOS distributions projected on the 1-propanol molecule for the configurations I-1 and I-2 (see Table V), we see that the second peak is the same for both configurations, but the first and third peaks are different which reflects the fact that the O-H bond direction for I-2 is by 180° rotated with respect to that of the configuration I-1. Comparing the DOS of the total slab, the partial DOS projected on the Si atoms as well as on the 1-propanol molecule

TABLE IV. Atomic composition of the highest-lying valence and lowest conduction bands for the configurations I-1, I-2, F-1, and F-2. In parentheses, the contributing atoms are indicated.

Bands	Main compositions
I-1-O1	$3p_z$ [up Si (A1,A2,A3)]
I-1-O2	$3p_x, 3p_x$ [up Si (A1-A4,B1-B4)], $3p_z$ [up Si (A4)]
I-1-U1	$3p_z$ [down Si (A1,A3,A4,B1-B4)]
I-1-U2	$3p_z$ [down Si (A1,A3,A4,B1-B4)] + $3p_z$ [Si in adjacent layer which form bonds with down Si (A1-A4,B1-B4)]
I-2-O1	$3p_z$ [up Si (A2)]
I-2-O2	$3p_z$ [up Si (A1,A3)]
I-2-U1	$3p_z$ [down Si (B1,B2,B3,B4)]
I-2-U2	$3s, 3p_z$ [down and up Si (B1,B2,B3,B4)]
F-1-O1	$3p_z$ [up Si (A1,A3,A4,B1,B3,B4)]
F-1-O2	$3s, 3p_z$ [up Si (B2)]
F-1-U1	$3p_z$ [down Si (A1,A3,A4,B1,B2,B3,B4)]
F-1-U2	$3p_z$ [down Si (A1,A3)], $3s, 3p_z$ [up Si (B2,B4)], $3p_z$ [down Si (B2,B4)]
F-2-O1	$3p_z$ [up Si (A4,B4)]
F-2-O2	$3s, 3p_z$ [up Si (A1,A3,B1,B3)]
F-2-U1	$3p_z$ [down Si (B1,B2,B3,B4)]
F-2-U2	$3p_z$ [down Si (A1,A3)]

(see Figs. 9 and 10) we find that near the Fermi level, the DOS is dominated by states that stem from the Si(001) substrate, but at low energy (far below the Fermi level), the total DOS is modulated by the profile of the 1-propanol admixture (or its fragments).

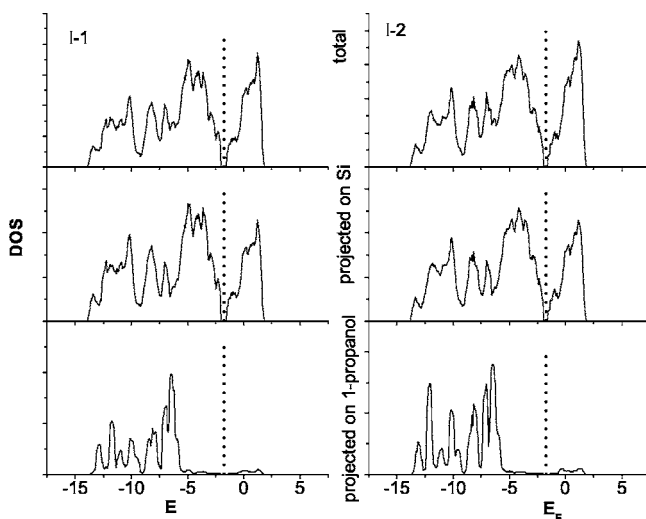


FIG. 9. The electronic DOS and partial DOS projected on Si and 1-propanol molecule for the physisorbed configurations I-1 and I-2 at 0.125 ML 1-propanol coverage. The vertical dotted lines represent the positions of the Fermi level.

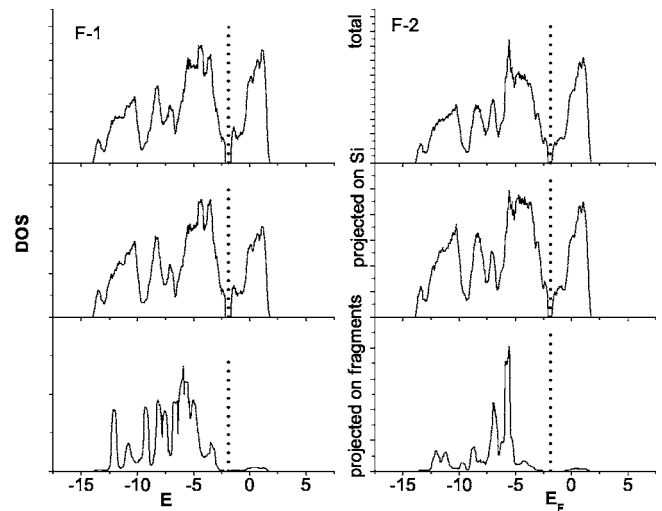


FIG. 10. The electronic DOS and partial DOS projected on Si and 1-propanol fragments for the chemisorbed configurations F-1 and F-2 at 0.125 ML 1-propanol coverage. The vertical dotted lines represent the positions of the Fermi level.

IV. DEPENDENCE ON THE LEVEL OF COVERAGE

Taking advantage of the slab approach, we will discuss in the following the dependence of the binding energy of the four basic configurations (I-1, I-2, F-1, F-2) on the coverage of the 1-propanol molecules. First, we will consider the basic configurations I-1, I-2, F-1, and F-2 with the coverage levels 1.00, 0.5, 0.25, and 0.125 ML, which corresponds to one 1-propanol molecule attached to one, two, four, and eight dimers, respectively. Table VI shows the binding energies of the four configurations of 1-propanol on the Si(001)-(2 × 1) surface.

Table VI shows that the binding energies per 1-propanol molecule for the physisorbed configurations I-1 and I-2 decrease with increasing coverage. This trend appears quite natural since increasing concentration of the adsorbed molecules on the Si(001) surface results in enhanced interaction between the molecules and hence weakens their bond with the substrate. The binding energy for the chemisorbed structure F-1 decreases with increasing coverage too. This may be related to the fact that the alkoxy fragment has similar transverse dimensions as the 1-propanol molecule. However, the binding energy for the chemisorbed configuration F-2 exhibits very little change with the variation of the coverage. This observation is ascribed to the strengthened interaction between the separated OH groups and their Si bonding partners.

The dependence of the energy barriers on the 1-propanol coverage in the interval [0.25 ML, 1.0 ML] is illustrated by Table VII, which contains the energy barriers E_b and transition state energy levels E_{TS} with respect to the energy of 1-propanol and Si(001) in isolation from each other. Two processes correspond to O-H bond and C-O bond scission.

Here we point out that the 1-propanol molecules are placed on the surface uniformly, and all the molecules dissociate simultaneously. From E_b values for the O-H and C-O bond rupture in Table VII, we find that the energy barriers

TABLE V. The main components of the peaks of the partial DOS distributions projected on the Si atoms and 1-propanol (or its fragments) for the configurations I-1, I-2, F-1, and F-2. The $3p$ represents $3p_x$, $3p_y$, and $3p_z$.

Configuration	Peak 1 position	Components of peak 1	Peak 2 position	Components of peak 2	Peak 3 position	Components of peak 3
Partial DOS (Si)	-3.0 to -5.0 eV	$3p$ (Si)	1.4 eV	$3p_x, 3p_y$ (Si)	-11.2 to -12.5 eV	$3p$ (Si)
I-1 partial DOS (1-propanol)	-11.7 eV	$2p_x, 2p_y$ (O)	-7.1 eV	$2p_z$ (C2,C3)	-6.4 eV	$2p_x$ (C3), $2p_y$ (C1)
Partial DOS (Si)	-3.0 to -5.0 eV	$3p$ (Si)	1.4 eV	$3p_x, 3p_y$ (Si)	-11.2 to -12.5 eV	$3p$ (Si)
I-2 partial DOS (1-propanol)	-12.1 eV	$2p_y$ (O)	-7.1 eV	$2p_z$ (C2,C3)	-6.5 eV	$2p_y$ (C2,C3)
Partial DOS (Si)	-3.0 to -5.0 eV	$3p$ (Si)	1.4 eV	$3p_x, 3p_y$ (Si)	-11.2 to -12.5 eV	$3p$ (Si)
F-1 partial DOS (H+alkoxy)	-9.3 eV	$2p_z$ (C1), $2p_x$ (O)	-6.7 eV	$2p_x$ (C3), $2p_y$ (O)	-6.1 eV	$2p_y$ (C3), $2p_z$ (C2)
Partial DOS (Si)	-3.0 to -5.0 eV	$3p$ (Si)	1.4 eV	$3p_x, 3p_y$ (Si)	-11.2 to -12.5 eV	$3p$ (Si)
F-2 partial DOS (OH+alkyl)	-12.5 eV	$2p_x, 2p_y$ (O)	-6.8 eV	$2p_y$ (C1), $2p_z$ (C3)	-5.5 eV	$2p_x, 2p_y$ (C2,C3)

for the O-H bond scission are only slightly affected by the level of coverage. However, the energy barriers for the C-O bond breaking (E_b) decrease with the increasing coverage.

From Table VI, the bonding of the chemisorbed structure F-1 (O-H bond scission) is weakened as the coverage increases, and Table VII reveals that the energy barrier with respect to the O-H bond rupture (E_b) becomes higher at 1.00 ML coverage. Thus, the probability of O-H bond scission is somewhat reduced at this level. On the other hand, the binding energy for the C-O bond cleavage changes very little as the coverage is varied, while the energy barrier with respect to the rupture of the C-O bond (E_b) has its minimal value at 1.00 ML. This suggests that at a high coverage level, a small amount of C-O cleavage might occur, as supported by the experimental observation at high surface coverage.⁹

The DOS distributions of the 1-propanol molecules (or its fragments) at the coverage levels considered in this work are shown in Fig. 11 for the physisorbed configurations I-1 and I-2, and Fig. 12 for the chemisorbed configurations F-1 and F-2.

TABLE VI. Binding energies of the adsorbate on Si(001) in eV/per 1-propanol molecule at four coverage levels.

Coverage	I-1	I-2	F-1	F-2
0.125	0.76	0.72	2.59	2.89
0.250	0.73	0.70	2.57	2.90
0.500	0.68	0.67	2.55	2.91
1.000	0.41	0.37	2.34	2.85

The partial DOS projected on the 1-propanol molecule for the physisorbed I-1 structure at 0.125 ML exhibits peaks at -6.4 and -7.1 eV which are traced back to $2p$ orbitals of the carbon atoms C1, C2, and C3, and the peak at -11.7 eV originates from the $2p_x$ and $2p_y$ orbitals of the oxygen atom. With increasing coverage the peaks at -6.4, -7.1, and -11.7 eV are found to grow if the substrate peak between -3.0 and -5.0 eV is taken as reference, which is the expected behavior upon 1-propanol deposition enhancement. This conclusion applies for all the physisorbed and chemisorbed configurations.

For more quantitative analysis of the DOS distributions, we examined the dependence of the energy gap on the 1-propanol coverage (or its fragments). Table VIII shows the obtained values for the physisorbed configurations I-1 and I-2, and the chemisorbed configurations F-1 and F-2 with 0.125, 0.25, 0.5, and 1.0 ML.

The energy gap for the Si(001)-(2 × 1) surface is 0.46 eV (see Table VIII), which is in keeping with experiment (the

TABLE VII. Energy barriers E_b and transition state energy levels E_{TS} , for the dissociation processes I-1 → F-1 and I-2 → F-2 at four levels of surface coverage. The reference for the indicated energy values is the energy of the separated subsystems.

Coverage	I-1 → F-1 (E_b)	I-1 → F-1 (E_{TS})	I-2 → F-2 (E_b)	I-2 → F-2 (E_{TS})
0.125	0.05	-0.70	1.34	0.62
0.250	0.02	-0.72	1.34	0.63
0.500	0.02	-0.65	1.32	0.65
1.000	0.05	-0.36	1.21	0.84

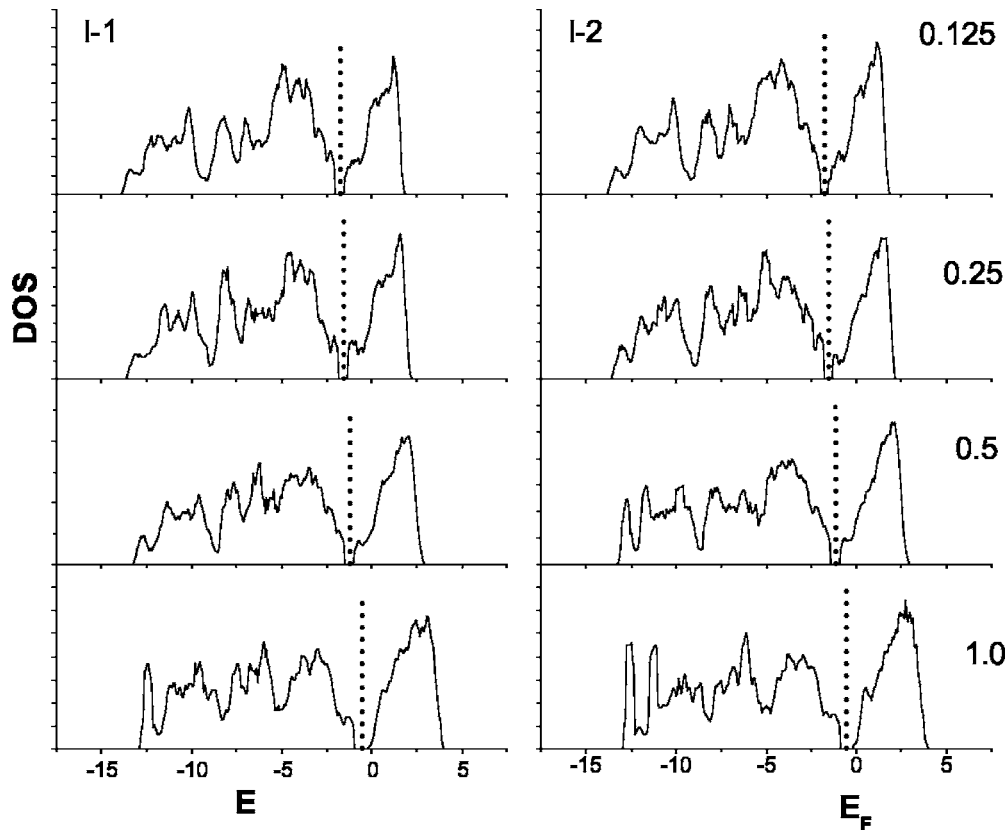


FIG. 11. The DOS of the full slab for the physisorbed configurations I-1 and I-2 at 0.125, 0.25, 0.5, and 1.0 ML.

corresponding experimental value³¹ is about 0.6 eV). The local DFT and GGA procedures tend to underestimate the energy gap of semiconductors by up to 25%.³² Table VIII shows that the energy gaps increase with the level of coverage, which reflects a growing degree of saturation of the silicon dangling bond as induced by the 1-propanol molecules. As a consequence of a higher number of oxygen atoms attached to the surface, and, by the same token, of dative bonds (for the physisorbed configurations I-1 and I-2) or covalent bonds (for the chemisorbed configurations F-1 and F-2) between oxygen atoms and silicon atoms, the surface turns increasingly insulating, i.e., the energy gap widens.

V. ROOM TEMPERATURE MOLECULAR DYNAMICS CALCULATIONS

The energy barrier computations have shown that the physisorbed 1-propanol molecule reacts with the Si(001)-(2×1) surface by cleavage of the O-H bond. Since the zero-temperature transition state analysis may not be able to access all of the relevant phase space volume, we perform a finite temperature *ab initio* MD simulation to take into account additional possible reactions at $T=300$ K. The 1×2 cell is adopted to carry out the MD simulation (the 2×2 cell was used as well, and the results from both approaches were found to agree). In the finite temperature MD calculations all atoms, including the passivating H atoms at the bottom of the slab, are allowed to move. In this manner, a large temperature gradient can be avoided. Lattice parameters are ex-

panded according to the temperature under study using the experimental thermal expansion coefficient in order to prevent the lattice from experiencing internal thermal strain.²⁰ The starting configuration is the physisorbed one I-1 (see Fig. 3); the O-H and O-C bond lengths are 1.01 and 1.48 Å, respectively. The I-1 physisorbed structure is heated to 300 K (room temperature) in 9000 MD step (9.0 ps, i.e., each step takes 1 fs), followed by another 3000 MD steps at 300 K to evolve the system under conditions of thermal equilibrium. Displaying the free energy of the system as a function of the evolution time, we assess if the system has reached its equilibrium. As illustrated by Fig. 13, the free energy fluctuates very little after 10 ps, which shows the system is at equilibrium. In Figs. 13–15, every data point represents an average result over an interval of 300 MD steps. In this way, high-frequency components due to thermal motion³³ are filtered out.

We consider the time variation of the O-C1 and Si-C1 bond lengths in the MD calculation, which are represented in Fig. 14. It is seen that the O-C1 bond is not ruptured in the process of the simulation. For times shorter than 6 ps, the distance between the C1 and the up Si atom fluctuates around 4.25 Å; between $T=6$ and 7 ps, it reduces by 1 Å, and after $T=7$ ps, it oscillates around 4.0 Å, which shows that no bond between C1 and the up Si is formed. This behavior rules out the chemisorbed configuration F-2 as an equilibrium structure.

On the other hand, the time variation of the O-H and Si-H bond lengths in the MD simulation, as drawn in Fig. 15, illustrates that before $T=6$ ps, the O-H bond length is about

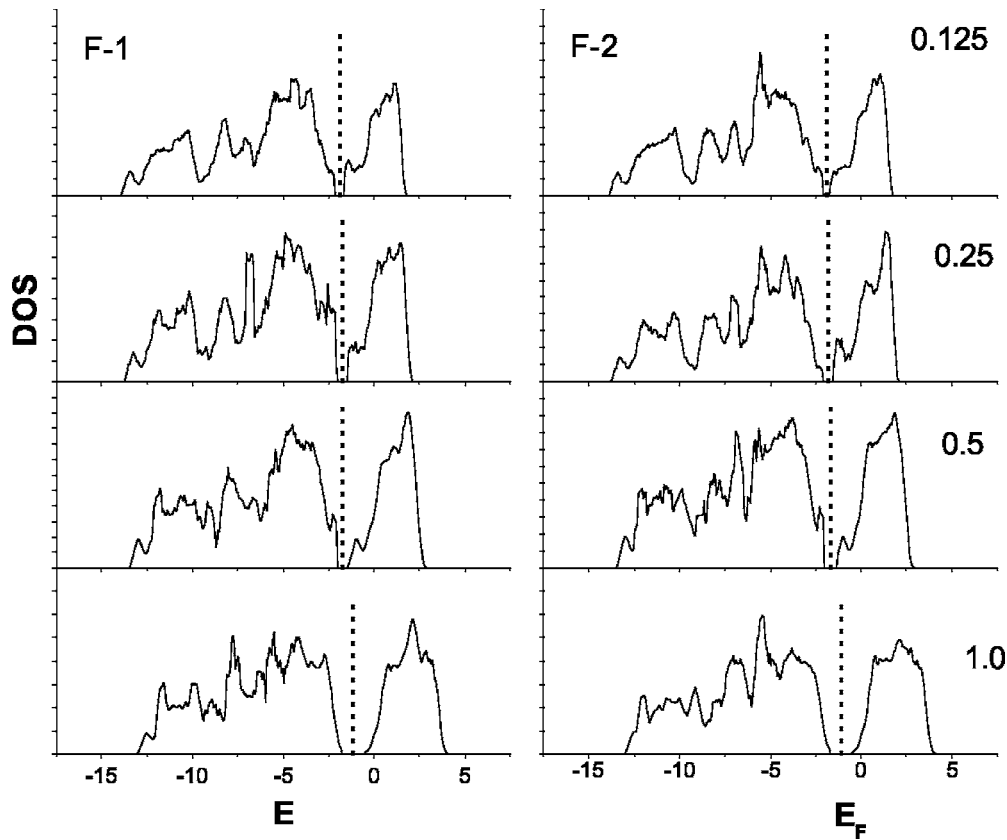


FIG. 12. The DOS of the full slab for the chemisorbed configurations F-1 and F-2 at 0.125, 0.25, 0.5, and 1.0 ML.

1.01 Å and the Si-H bond length oscillates around 2.25 Å. In the period of 6–7 ps, the O-H bond length elongates up to 3.75 Å, and the Si-H bond length shortens to 1.48 Å. This marked change indicates a transition from the metastable physisorbed phase I-1 to the “stable” chemisorbed phase F-1. The characterization as stable for the F-1 structure only makes sense at room temperature, since the chemisorbed phase F-2 is much more stable than F-1 at still higher temperature. After 7 ps, the O-H bond length oscillates with decreasing amplitude, and the Si-H bond length reaches its equilibrium value of 1.48 Å. Figure 15 shows that O-H bond scission occurs and the Si-H bond forms between $T=6$ and 7 ps. The equilibrium structure is the chemisorbed configuration F-1, i.e., the O-H bond is broken (see Fig. 4), which is consistent with the energy barrier calculation at zero temperature.

Inspection of the MD simulation results shows that the O-H bond is broken. The H atom is detached and reattaches

TABLE VIII. Energy gaps ΔE (eV) of the Si(001)-(2×1) pure surface compared to those of the 1-propanol adsorption structures I-1, I-2, F-1, and F-2 on Si(001) at four levels of coverage.

Coverage	Si surface	I-1	I-2	F-1	F-2
0.125	0.46	0.53	0.40	0.53	0.40
0.250	0.46	0.53	0.47	0.60	0.60
0.500	0.46	0.53	0.53	0.80	0.73
1.000	0.46	0.80	0.73	1.27	1.20

to the “up” silicon atom of the same dimer (dimer A2) to form a new H-Si bond. After 7 ps, all atoms oscillate around their stable equilibrium positions. Another method of performing the MD simulations consists in setting an initial temperature T equal to 300 K without any heating and letting the system evolve at this temperature. Following this avenue, we arrive at the same conclusions as reported above.

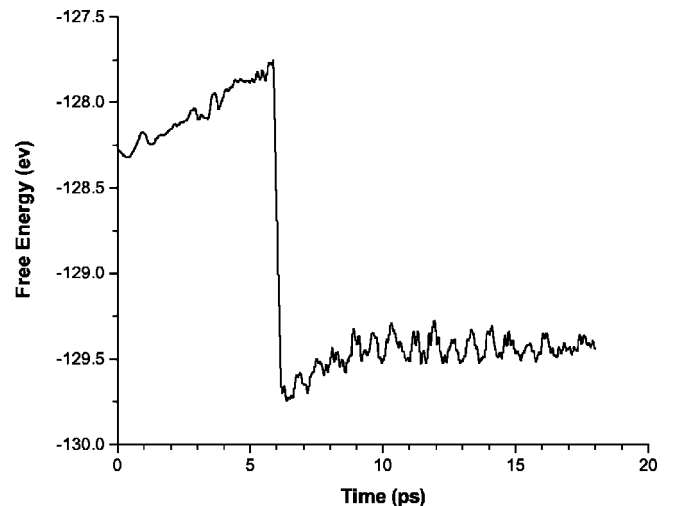


FIG. 13. Time variation of the free energy in the MD simulation. An average over every 300 MD steps has been taken to filter out high-thermal-frequency components.

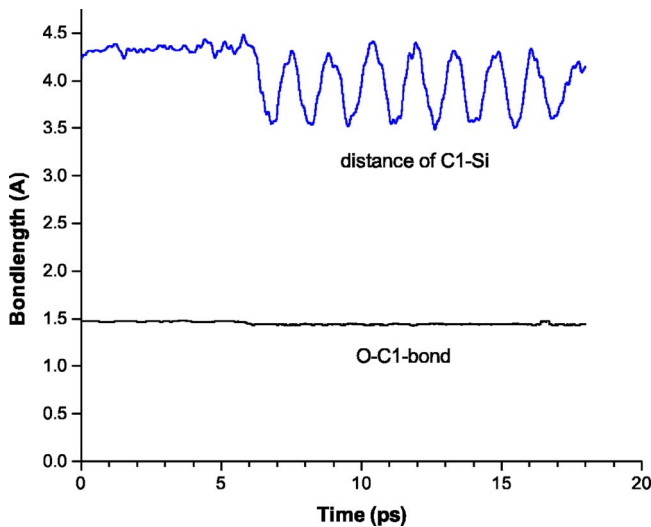


FIG. 14. (Color online) Time variations of the Si-C1 distance and O-C1 bond length in the MD evolution. An average over every 300 MD steps has been taken to filter out high-thermal-frequency components.

VI. SUMMARY

We have performed a study on the physisorption and chemisorption of 1-propanol molecules on the Si(001)-(2×1) surface from first principles. Phenomena related to the geometric, electronic, energetic, and fragmentation pathways have been investigated within three-dimensional periodic boundary conditions. Specifically, we have shown that the 1-propanol molecule initially interacts with the Si surface through formation of a dative bond. Subsequently, the physisorbed 1-propanol molecule reacts with the surface by cleavage of either the O-C or the O-H bond. The O-C bond

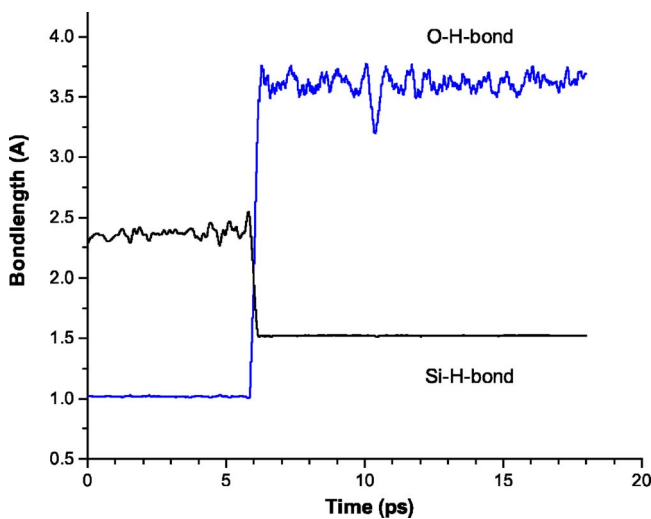


FIG. 15. (Color online) Time variation of the O-H and Si-H bond length in the evolution where O-H bond is breaking and Si-H bond is forming. An average over every 300 MD steps has been taken to filter out high-thermal-frequency components.

cleavage is thermodynamically stable, but the O-H bond cleavage is kinetically favored. We characterized the geometric modification of the Si(001)-(2×1) surface in response to physisorption as well as chemisorption, which cannot be described by use of a single-dimer cluster model.

We have first calculated the band structure and the DOS for four configurations, demonstrating that the occupied bands within the fundamental band gap of the silicon are composed of the up Si atoms, and the unoccupied bands originate from the down Si atoms. No conduction band within the fundamental band gap could be associated with Si-O bonding. This feature distinguishes the present case from that of acetonitrile adsorption on the silicon surface.¹⁹ For acetonitrile adsorption, a conduction band within this gap has been assigned to Si-N bonding, which shows that the acetonitrile electronic interaction with the silicon substrate might be stronger than that of 1-propanol. The peaks around the Fermi level and other peaks related to adsorption for the DOS and partial DOS distributions were discussed. It has been shown that the DOS near the Fermi level is dominated by the states from the Si(001) surface, but at low energy (far below the Fermi level) the DOS is modulated by the 1-propanol contribution, or that of its fragments.

We have analyzed the dependence of the various properties (binding energy, energy barrier, DOS, energy gap) for the configurations I-1, I-2, F-1, and F-2 on the coverage levels 0.125, 0.25, 0.5, and 1.0 ML. From this research, the binding energies of the physisorbed configuration I-1, I-2, and chemisorbed configuration F-1 decrease with increasing coverage. This trend appears plausible since increasing concentration of 1-propanol molecules on the Si(001) surface results in enhanced repulsion between the molecules and hence destabilization. However, the binding energy for the chemisorbed configuration F-2 is found to be rather insensitive to the variation of the coverage level. The energy barrier with respect to O-H bond scission at four levels of coverage changes slightly, and reaches its maximum within the [0.25 ML, 1.0 ML] interval at 1.00 ML. However, the energy barriers with respect to the C-O bond rupture (E_b) decrease with increasing coverage. Thus, we found the bonding of the chemisorbed structure F-1 (O-H bond scission) destabilized at higher coverage, while the energy barrier is highest at 1.00 ML, suggesting a reduced probability of O-H bond scission at the 1.00 ML level. On the other hand, the binding energy for the C-O bond breaking structure changes very little with the level of coverage, while the energy barrier with respect to the C-O bond rupture (E_b) adopts its minimal value at 1.00 ML. One concludes that conditions of high coverage favor C-O cleavage, and a small admixture of this chemisorption channel may be observable at 1.0 ML.⁹ The DOS showed that upon increasing 1-propanol deposition, the peaks due to the 1-propanol molecular orbitals grow in intensity, and the substrate features diminish. Also, with enhanced coverage, the energy gaps widen which indicates increasing saturation of the silicon dangling bonds by the 1-propanol molecules. The planar 1-propanol density on the Si(001) surface thus represents a parameter that allows to

alter the nature of the surface from semiconducting to insulating.

Finally, recording the time variation of the O-H and Si-H bond lengths by means of *ab initio* MD simulation demonstrated that the O-H bond length is spontaneously ruptured at room temperature, and the dissociated H atom forms a Si-H bond. The final equilibrium structure at room temperature is the chemisorbed configuration F-1. The observed O-H bond rupture is in accordance with the energy barrier calculation at zero temperature.

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