

Ab Initio Study of Chemisorption Reactions for Carboxylic Acids on Hydrogenated Silicon Surfaces

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We study chemisorbed configurations of C₃H₆O₂ on the extended H:Si(100) surface, through first-principles density-functional calculations in a supercell approach. We demonstrate that oxygen-bonded organic monolayers on this silicon substrate is thermodynamically very stable, and comparing several Si–O–C and Si–C linked configurations, we find that the doubly-O-bonded configuration is favored and should lead to ordered SAMs. We find, moreover, that the Si–O–C bridge in this case does not block charge transfer from surface to molecule.

The quest for organic functionalization of silicon surfaces¹ is part of an effort to devise novel semiconductor-based materials to be used in advanced technological applications, for instance, in hybrid (bio)molecular devices. In the case of Si surfaces, either clean or oxidized, to obtain covalently-bonded self-assembled monolayers (SAMs) from organic molecules one traditionally resorts to siloxane chemistry, leading to the formation of Si–O bonds. The resulting monolayers have some undesirable properties such as disorder and reduced SAM reproducibility.² Directly Si–C linked monolayers provide stable functionalization of the surfaces,^{3,4} however, typically require surface activation.¹ Several properties of Si–C linked monolayers, such as coverage and tilt angle, were assessed^{3,5} on different Si substrates, ranging from amorphous silicon to the ordered (100) and (111) free and hydrogenated silicon surfaces. The H:Si surfaces are of special interest because of their higher resistance to oxide formation; however, it is known that surface defects and even a modest presence in the environment of impurities containing oxygen, such as O₂ and H₂O, can prevent the formation of ordered alkyl monolayers.⁶ Moreover, once present the strong Si–O surface bond cannot be broken by means of the typical techniques employed in the hydrosilation reactions.⁷ The direct formation of Si–O–R layers from thermal reactions of alcohols (R–OH) and aldehydes (R–C=O) with H:Si(111) was also thoroughly investigated⁸ and the resulting Si–O bond turned out to be fairly stable. Characterization of SAMs resulting from stable Si–O linked monolayers revealed smaller tilt angles⁹ and higher coverage¹⁰ than in Si–C-bonded monolayers.³ However, the actual mechanism governing the chemisorption reaction was not unambiguously recognized. Chemical reactions between molecules and surfaces of electronic materials can be very different from the corresponding solution–ion transformations¹¹ because the surface electronic structure can radically modify the reaction mechanisms of molecular chemistry. Thus, even thorough theoretical studies based¹² on force-field methods (non reactive and parametrized for the molecular environment) or ab initio calculations based on model

clusters of too-few atoms can be inadequate for an understanding of the specific reaction mechanism. We present here the first ab initio study of the chemisorption of monolayers of carboxylic acids on extended hydrogenated silicon surfaces¹³ to understand whether and when the oxygen atom in the reactive COOH group is conducive to the self-assembling process by acting as a hook between the organic molecule and substrate. We use as a model molecule propionic acid, C₃H₆O₂, which is short enough for a careful theoretical study, yet long enough to allow for realistic modeling. We focus on the dihydride-terminated silicon surface H:Si(100)1 × 1, which allows for a double-O bridge reaction with propionic acid: this configuration was never previously addressed, to our knowledge, by studies of the reaction between organic acids and H–Si surfaces.^{5,11,14} The fact that the carboxylic group COOH contains both the carbonyl (C=O) and the hydroxyl (OH) terminations provides a variety of chemisorption reactions with the hydrogenated surface, and thus we are able to study and compare the two typical bonds Si–C and Si–O–C. From our ab initio calculations, we propose that the energetically favored configuration is the double bridge involving both O atoms of the COOH group.

The H:Si surface is simulated in a supercell geometry with 4 Si atoms per layer, 6 Si layers, H-saturated on both the front and back sides. One side of the surface is then reacted with 1 or 2 identical molecules, simulating 0.5 or 1 monolayer (ML) (50% or 100%) coverage. A laterally larger cell is also used for 0.25 ML coverage. Our calculations¹⁵ are performed from first principles within the density functional theory scheme,¹⁶ testing both LDA and PW91 exchange–correlation functionals;¹⁷ we use ultrasoft pseudopotentials¹⁸ with plane wave basis set expanded to 25 Ry energy cutoff, and 16 irreducible Monkhorst–Pack¹⁹ points for *k*-space integration. Due to the complexity of the systems under study, the input configurations are obtained using the PCFF empirical force field;²⁰ ab initio structural relaxations are then performed until the forces vanish within 0.005 eV/Å.

We studied the energetics at *T* = 0 of several possible reactions for the COOH group on the perfectly hydrogenated surface (see Figure 1, far left panel). The proposed reactions can lead either to the formation of Si–O–C bonds, with the oxygen atoms in a bridge position between the carbon

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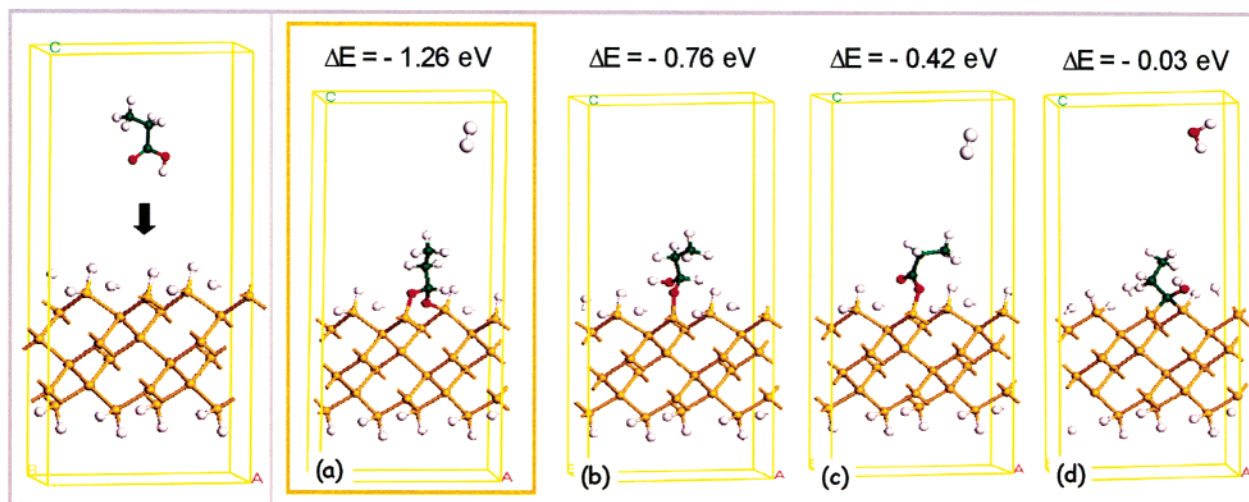


Figure 1. Representation of the relaxed structure of reagents and products for the chemisorption of propionic acid $C_3H_6O_2$ on $H:Si(100)$, in the 50% coverage regime. The panel on the far left shows the initial reagents. Panel: (a) double-oxygen bridge configuration plus H_2 ; (b) single-oxygen bridge through the carbonyl group; (c) single-oxygen bridge through the hydroxyl group plus H_2 ; (d) direct $Si-C$ link plus H_2O . Reaction occurs through the carboxylic group.

atom of the carboxylic group and the silicon atoms of the hydrogenated surface, mostly releasing a hydrogen molecule, or to the formation of a direct $Si-C$ bond, with a water molecule as residue. None of these reactions necessarily requires any prior surface activation mechanism. The relaxed geometries of the reagents are represented in the leftmost inset of Figure 1, and the most significant chemisorbed configurations, which correspond to exothermic reactions within our calculations, are represented in the other four insets. We obtain the binding energy for the chemisorption reaction by taking the difference between the calculated total energy of reagents (isolated propionic acid + hydrogenated surface) and reaction products (chemisorbed configuration + residue). The analysis of the binding energies for all relevant reactions indicates that the most stable configuration is characterized by two strong $Si-O-C$ bonds involving two Si atoms of the semiconductor substrate, the two O atoms, and the C atom of the $COOH$ group (Figure 1b) that becomes tetrahedrally coordinated. The adsorption energy is 1.26 eV, as compared to 0.76 eV for the next-stable configuration (both the PW91 and LDA calculations give similar values). The chemisorption of the carboxylic group leading to a direct $Si-C$ bond (Figure 1d) is not energetically favorable.

For the doubly-oxygen-bonded configuration the highest molecular packing corresponding to 1 ML coverage is slightly preferred over the 0.5 and 0.25 ML coverage, by 0.03 and 0.05 eV/mol, respectively, whereas in the case of the $Si-C$ -bonded configuration the 1 ML coverage is definitely unstable. These results are in qualitative agreement with experimental determination of coverages in the $Si-O-C$ and $Si-C$ linked configurations.^{3,10} The chemisorption reaction involving dimer molecules of propionic acid, typical of the gas phase,²¹ was also addressed: our results indicate that the doubly-oxygen-bridged configuration remains energetically favorable.

We now analyze the electronic properties of the molecule-surface bond, in the 50% coverage, focusing on the configuration with the double $Si-O$ bond.

The corresponding density of states (DOS) is reported in Figure 2, compared to the DOS of the clean $H:Si$ surface and of the isolated molecule. The origin of the energy scale $E_v = 0$ eV corresponds to the top valence state of the clean hydrogenated surface. The energy line-up between states of functionalized and clean surfaces is done by aligning the hydrogen peak

of the backside of both surfaces (this peak corresponds to localized surface states, not affected by the functionalization at the front side). The energy line-up between the functionalized surface and the isolated molecule is obtained by searching in both configurations for molecular states not affected (density-wise) by the chemisorption. This is the case of the fourth state at -11.71 eV, used for the alignment. The four lowest energy peaks in the DOS of the functionalized surface are fully localized on the adsorbed radical. In particular, the two lowest peaks are mainly built from s-type states of the carboxylic group (Figure 2a), which we find experience a large energy shift with respect to the molecular levels of the isolated molecule by respectively 1.03 and 0.70 eV. This semi-core level shift can be attributed to the modification of the orbitals involved in the adsorbate-substrate bond: in the chemisorbed configuration, the C atom formerly belonging to the $COOH$ group assumes a tetrahedral coordination, and both O atoms modify their bonding geometry. This general phenomenon of structure modification is present to a lesser extent in singly-O-bonded configurations.

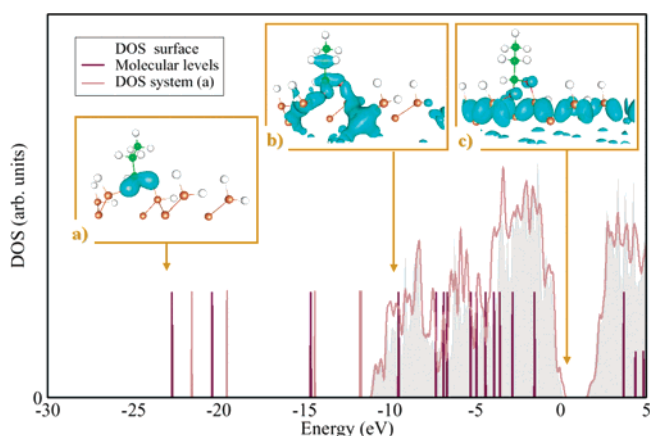


Figure 2. Total density of states of propionic acid $C_3H_6O_2$ chemisorbed on $H:Si(100)$, in the double-oxygen bridge configuration, compared to the clean hydrogenated surface (shaded region) and the isolated molecule. The insets, reading from the left to the right, represent significant single-particle states of the functionalized surface: (a) the lowest energy orbital, which maintains a molecular character; (b) a bonding low-energy orbital; (c) the resonant valence-top state.

In the case of a direct Si–C bond the two semi-core levels join together in a single one, because of the release of one O atom within the residual H₂O. This effect can be used to probe experimentally the bonding configuration. The Fermi level of the hydrogenated surface is hardly affected by functionalization, and we find that the HOMO (highest occupied molecular orbital) of the isolated molecule aligns at -1.52 eV. Each molecular state interacts with s- and p-type states of the hydrogenated surface (mainly those closer in energy), forming hybrid orbitals that carry, however, some memory of the originating orbitals. The analysis of the single particle electron states shows the broad formation of bonding orbitals, as depicted in Figure 2b, whose presence in the low-energy range is a signature of the strong attachment of the molecule to the substrate. The bond structure is complex and involves the cooperation of different atoms of the adsorbate in addition to the directly-bonded one. We also observe resonant states, originating from the superposition of molecular states and the dispersive silicon surface band states, involving Si atoms from subsurface layers, and an unexpected feature is that the top valence state (Figure 2c) shows a resonance between the p-type orbitals centered on oxygen atoms and states from the first Si surface layer. The occurrence of bonding states covering the entire adsorbate up to 1 eV below the Fermi energy and resonant states even beyond this level suggests that the Si–O–C bond does not limit the electronic coupling between Si and organic fragments: indeed, the analysis of Lowdin charges confirms charge transfer from the semiconductor substrate to the molecules.

In conclusion, our first-principles calculations show that the doubly-oxygen-bonded attachment corresponds to the most stable configuration resulting from the chemisorption reaction of carboxylic acids on a H:Si(100)1×1 surface. We find also that this configuration aids ordering of the SAM, as it favors the full coverage 1 ML regime. Furthermore, because full coverage should sterically inhibit the intrusion of oxygen-containing impurities, so-constructed Si–O-bonded monolayers should be extremely stable. We point out that the O-bridge does not block charge-transfer between surface and molecule, making this configuration ideal for hybrid devices.

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