Computational and Theoretical Chemistry 1073 (2015) 106–115

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

A comparative chemisorption study of acrylic, vinyl acetic, fumaric, maleic and tartaric acid on $Si(100)2 \times 1$ by van der Waals corrected DFT

Marilena Carbone

Dept. of Chemical Science and Technologies, University Tor Vergata, Via della Ricerca Scientifica, 1 00133 Roma, Italy

ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form 21 September 2015
Accepted 21 September 2015
Available online 28 September 2015

Keywords:
Adsorption energy
Silicon surface
Multifunctional carboxylic acids
DFT
Van der Waals forces

ABSTRACT

The comparative chemisorption of multifunctional carboxylic acids on $Si(100)2 \times 1$ has been investigated by van der Waals corrected DFT. Several configurations with one or more functional groups involved in the binding process were considered for acrylic, vinyl acetic, maleic, fumaric and tartaric acid both in meso and in chiral form. In general, the dissociative adsorptions are more favourable than the molecular ones. The comparison between uni- and bidentate configurations indicates that the latter is the more favourable for all except for vinyl acetic acid, for which the unidentate on top adsorption is preferred. C=C [2+2] cycloadditions are less stable when a second carboxylic group is present and in general are less favourable than Si—O linkages. Adsorption through hydroxyl groups is on average slightly less stable than through carboxylic groups. The most stable configuration is obtained with the adsorption through two groups bridging two dimers along a line, by meso tartaric and maleic acid. The simultaneous binding through three functional groups decrease the adsorption energy, whereas the linkage through four functional groups makes the adsorbate unstable. Molecular adsorption such as C=O [2+2] cycloadditions and hydroxyl dative bonds have small adsorption energies.

1. Introduction

Organic functionalization of semiconductor surfaces has attracted recent interest due to its scientific and technological importance and potential applicability to molecule-based devices, bio-sensors, and organic dielectrics [1–8]. Furthermore, electrochemistry, microelectronics, Metal–Oxide–Semiconductor Field-Effect Transistors (MOSFETs) [9–11] are all based on the interaction of molecules with semiconductor surfaces.

Organic molecules such as unsaturated and aromatic molecules, alcohols, carboxylic acids and amines have been investigated for their reactivity with semiconductor surfaces [12–16]. Cycloaddition has been established as the adsorption mechanism of unsaturated hydrocarbons on Si or Ge surfaces [17–24]. The attachment of alcohols [25–32], and acids [33–37] to semiconductor surfaces occurs, instead, through Lewis acid-base reactions. An ordered and selective surface structure, such as the $Si(100)2 \times 1$ is essential for employing functionalized semiconductors in molecular electronics devices. In view of building up molecular circuits on silicon surfaces, multifunctional molecules may be used for adsorption on semiconductor surfaces, with one functional group envisaged as anchoring site to the surface, and the remaining one enabling the surface growth, as in the spontaneous urea coupling reaction on Ge(100) [38]. The potential applications of multifunctional molecules as base units for surface circuits largely depend on the relative reactivity of the functional groups with respect to the selected surface. Cycloadducts are the most stable products of adsorption of unsaturated hydrocarbons conjugated with aromatic or hetero-aromatic rings, such as styrene [39], phenylacetylene [40] and vinyl thiophene [41] on the $Si(100)2 \times 1$ surface. In all these cases, the preferential adsorption geometry is on top of a surface dimer. The relative reactivity follows a different order for the alkenes conjugated to oxygen-containing functional groups. Combined experimental and computation studies of allyl alcohol [42], allyl aldehyde [43] and acrylic acid [44] (allyl carboxylic acid) indicate a preferential adsorption through the oxygen atoms, rather than via cycloaddition of the double bond. The adsorption through Si—O linkage is preferred over the formation of the cycloadduct also for a non-conjugated alkene-alcohol such as cis-2-butene-1,4-diol on $Si(100)2 \times 1$ [45]. In the most stable configuration, the molecule adsorbs on a Si dimer via dual Si—O bonding after O—H dissociation, forming a bridged structure. This sort of "arch" leaves the double bond easily accessible for further reactions. The adsorption of amines conjugated with an alcohol such as allylamine [46] proceeds via unidentate adsorption through the nitrogen atom on $Si(100)2 \times 1$. At variance with this, the adsorption

---

E-mail address: carbone@uniroma2.it

http://dx.doi.org/10.1016/j.comptc.2015.09.019
2210-271X/

on Si(100) occurs preferentially through Si—C bond (via saturation of C═C to form a unidentate adstructure) [47]. In a systematic investigation on amino acids adsorption on Si(100)2 × 1, performed excluding solvation effects, a preferential adsorption through the oxygen rather than the nitrogen atom is found on kinetic ground, due to a nearly barrierless adsorption process [48].

In this paper, the relative reactivity of several multifunctional carboxylic acids with respect to Si(100)2 × 1 is examined via van der Waals corrected DFT investigations of the chemisorbed species. In particular, the adsorption configurations are considered of acrylic acid (prop-2enoic acid, $C_3H_4O_2$), vinyl acetic acid (but-3-enoic acid $C_4H_4O_2$), fumaric acid (trans-butendioic acid, $C_4H_4O_4$), maleic acid (cis-butendioic acid $C_4H_4O_4$) and tartaric acid (2,3 dyhydroxybutanedioic acid $C_4H_6O_6$), both in diasteroisomeric (chiral) and in the meso (achiral) form. The aim is at comparing the effects of the mutual positions of functional groups on the adsorption properties and possible further reactivity for a series of carboxylic acids. Therefore, the chosen adsorbates are mono- or dicarboxylic acids associated or conjugated with terminal alkenes, central alkenes in cis and trans configurations as well as with hydroxyl groups in central positions. This investigation is, to some extent, predictive, since experimental and computational literature has been reported for acrylic and vinyl acetic acid [44,58,59], but so far no data appear to be available on the adsorption of the chosen dicarboxylic acid on Si(100)2 × 1.

2. Method

Periodic Density Functional Theory. All electronic structure calculations were performed using the periodic density functional theory and the ultrasoft Vanderbilt pseudopotential method within the generalised gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) for the exchange–correlation functional. This method is implemented in the plane-wave self-consistent field (Pwscf) code in the Quantum-ESPRESSO open-source distribution, version 5.0. Kinetic-energy cutoffs for wave functions and charge density were 408.1 eV (30 Ry) and 2856.7 eV (210 Ry), respectively; this converges the total energy within 0.01 eV/atom. The *p* (2 × 2) reconstructed Si(100) surface was modeled by means of repeated slab supercells containing 10 atomic layers, with four rows of two alternating buckled dimers on each (100) face (made parallel to the xy plane). At the bottom surface of the supercell, all Si atoms are passivated by H atoms. All the atoms except the bottom Si and H layers were allowed to relax. The vacuum region between supercells was about 14 Å in the *z*-direction. The surface size and vacuum region ensure the optimisation of the adsorbed molecules, regardless of the starting position with respect to the surface. It was verified that, by starting with the unreconstructed, clean Si(100) surface, the optimisation procedure correctly reproduces asymmetric surface dimers, with a dimer bond length and a buckling angle in good agreement with previous highly converged *ab initio* calculations. The sampling for the Brillouin zone includes a mesh of 2 × 2 × 2 special *k*-points of the Monkhorst–Pack scheme.

In the computation of organic molecules adsorption on a semiconductor surface it was taken into account that the dispersion interactions may play a role. Johnston et al. [49] compared two adsorption configuration of benzene on Si(100) by using several exchange and correlation functionals and found that the identification of the most stable one depended on the inclusion of van der Waals forces (vdW). Recently, Arefi et al. [50] reported a detailed study on alkyl chains adsorbed on Si(100) surface where the adsorption configurations were computed by DFT both with and without the vdW interaction and compared against experimental results, the best match including vdW forces. In particular, they used the quantum espresso package and opted for the Waals density functional (vdW-DF2) which shows a better agreement with accurate quantum chemical calculations on 22 duplexes [51].

In the current paper, long range interactions were included by using self-consistent DFT-DF2 as suggested by Grimme [52] and implemented within quantum espresso framework [53–56].

The adsorption energies (E_{ads}) are calculated as follows:

$$E_{\text{ads}} = -(E_{\text{adsorbed}} - E_{\text{clean}} - E_{\text{free molecule}}),$$

where the convention is used that an exothermic adsorption process produces a positive value for its adsorption energy (AE).

3. Results and discussion

The adsorption of multifunctional molecules may occur selectively through one functional group only or employing more functional groups simultaneously. In either case, the stability of the final configurations, as well as the functional groups left free for further interactions change.

In this paper, the adsorption on Si(100)2 × 1 of four different multifunctional carboxylic acids, i.e. acrylic (AcA), vinyl acetic (VAA), tartaric in the meso (M-TaA), and SD form (SD-TaA), fumaric (FuA, trans and MaA maleic/cis isomer) is comparatively investigated by DFT. All molecules possess a terminal carboxylic group and vary for the alkyl chain length, the number, type (alcohol, double bond and/or another terminal carboxylic group) and conjugation of additional functional groups. A sketch of the reconstructed Si(100)2 × 1 surface and of the selected multifunctional carboxylic acids is presented in Fig. 1. In choosing the starting models for the geometrical optimisations it was considered that the functional groups of the selected molecules may adsorb either molecularly or dissociatively. In the case of alcohols, both molecular and dissociative adsorption occurs through the interaction of the hydroxylic oxygen with a surface silicon atom, though in the former case the hydroxylic hydrogen atom remains bonded to the oxygen (to form a dative bond), in the latter it binds to another silicon surface atom. Furthermore, the alcohol dative bond may be evaluated as precursor of the dissociative one [57,58]. The adsorption through carboxyl functional groups may be quite complex as the carboxylic group is considered intrinsically multifunctional, with a carbonyl double bond (C═O) which may give a molecular [2+2] cycloaddition on silicon surfaces and the hydroxyl group which may give rise to both dative and dissociative bonds. Furthermore, due to the proximity of —C═O and —OH groups, the dissociative adsorption may be unidentate and bidentate, with the breakage of one O—H bond and the formation one Si—H bond and one or two Si—O bonds [37,44,59,60]. In general, both experimental and theoretical studies indicate that the preferential adsorption of oxygen containing molecules such as alcohols and carboxylic acids on silicon surfaces occurs dissociatively, with breakage of O—H bonds and formation of Si—O bonds [16,26,32,34,45,61,62].

The type of adsorption of alkenes (as well as alkynes and aromatic molecules) on silicon surfaces has been long investigated and evidences point at a molecular [2+2] C═C adsorption, though the adsorption mechanism may depend on the chain length of the alkene [63–66].

When bi- or multifunctional molecules are adsorbed on a silicon surface, it is important to establish which the preferential interacting groups and modes are. This was done, for instance for styrene [39] and vinyl thiophene [41] on Si(100)2 × 1, where the comparison was made between the reactivity of aromatic and alkene functionalities. In the case of phenol, instead the reactivity was compared in terms of molecular versus dissociative adsorption on Si(100)2 × 1 [67]. In the current paper, in order to compare the reactivity of multifunctional carboxylic acids, both dissociative and