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Conformation-selective adsorption of 2,3-butanediol on Si(0 0 1)

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Abstract

The adsorption of 2,3-butanediol on the Si(0 0 1) surface is studied by means of *first-principles* pseudopotential calculations. Molecular adsorption on top of the Si dimers resulting in a 6-membered ring of the O–C–C–O segment with the dimer atoms is energetically favored, in agreement with the interpretation of recent experiments. The adsorption energy difference for butanediol adsorbed in either gauche or anti conformation is nearly one order of magnitude larger than the energy difference between the respective conformers in gas phase, pointing to a conformation-selective adsorption.

Keywords: Silicon surface; Alcohols; Density functional calculations; Chemisorption

The chemistry of small organic molecules on semiconductor surfaces is of both fundamental and technological interest [1–3]. This interest arises from the vast range of qualities that organic molecules can be designed to have, and the hope of adding their functionality to semiconductor technology. Of particular interest are therefore surface reactions with polyfunctional organic molecules.

As an example for the adsorption of diols on semiconductor surfaces, Kim et al. [4] have recently studied the reaction of 2,3-butanediol ($C_4H_{10}O_2$) with the Si(0 0 1) surface using photoelectron spectroscopy. 2,3-Butanediol is a small molecule containing two hydroxyl (–OH) groups which is interesting from the stereo-chemical point of view. Firstly, it is chiral: The carbon atoms bonded to –OH groups are chiral centers. Secondly, because rotation around a single C–C bond is relatively free, the molecule exists in a large variety of confirmations. Not all of them are suitable for adsorption on Si(0 0 1): If the bonding

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is to occur via the hydroxyl groups, these should for steric reasons be in gauche conformation. Anti conformation of the hydroxyl groups should not occur. However, the orientation of the methyl groups seems to remain as degree of freedom. Fig. 1 shows ball-and-stick models and Newman projections for the energetically favored $g^-G^-g'^+$ (CH_3 gauche) and g^-G^+t' (CH_3 anti) conformers of (*R*,*R*)-2,3-butanediol [5,6]. According to B3LYP/6-31G* calculations [5], the gauche conformation, with a dihedral angle between the methyl groups of about 60°, is slightly (by 19 meV) more stable than the anti conformation. We focus on these two conformers in our adsorption study.

The calculations are performed using the Vienna Ab-initio Simulation Package (VASP) implementation [7] of the gradient-corrected density functional theory (DFT–GGA) [8]. The electron–ion interaction is described by non-normconserving ultrasoft pseudopotentials [9]. We expand the valence wave functions into plane waves up to an energy cutoff of 25 Ry. The Brillouin zone integrations are performed using sets corresponding to 64 **k** points in the full (1×1) surface Brillouin zone. All calculations are performed using the calculated Si equilibrium lattice constant of 5.456 Å. The surface structure is considered to be in equilibrium when the forces are below 50 meV/Å. To calculate the density of state, the energy spectrum is Gaussian broadened by 0.2 eV.

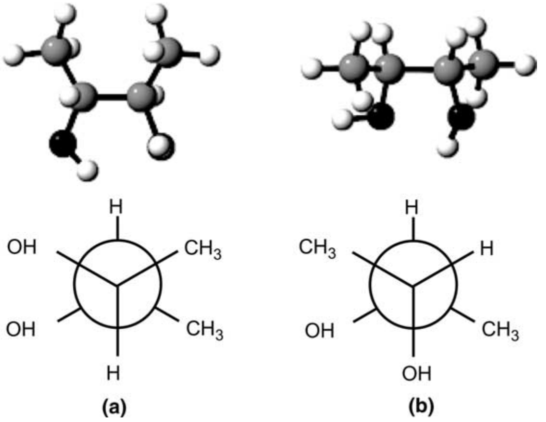

Fig. 1. Ball-and-stick models and Newman projections for (a) the $g^-G^-g'^+$ and (b) the g^-G^+t' conformers of (*R*,*R*)-2,3-butanediol. Black, gray and white balls indicate O, C and H atoms, respectively.

The surface is modeled with a periodically repeated slab, consisting of 12 atomic Si layers plus adsorbed butanediol. We use supercells with $p(4 \times 2)$ and $p(2 \times 2)$ or $c(4 \times 2)$ surface periodicities for studying coverages of 0.25 and 0.5 monolayers (ML), respectively. Here 1 ML is defined as one molecule adsorbed per Si surface dimer. The topmost five layers of the slab as well as the adsorbed molecules are allowed to relax.

Calculations for gas-phase 2,3-butanediol were performed using a $18 \times 18 \times 18$ Å^3 supercell and enforcing a force limit of 5 meV/Å. In agreement with Ref. [5], we find the gauche to be favored over the anti conformer. The calculated energy difference of 41 meV is somewhat larger than the result of Ref. [5], however. Intramolecular H···O–H hydrogen bonds between the two hydroxyl groups are formed. The predicted bond lengths are 2.12 and 2.30 Å for the gauche and anti conformers, respectively.

Alcohols adsorb on Si(001) by a dissociative reaction via the hydroxyl groups [10–14]. Ethanol, for example, first forms a dative bond, before either an O–H or an O–C cleavage occurs [13]. The energy barrier of the latter reaction renders the hydrogen dissociation more likely at room temperature. A similar reaction is found for water adsorbed on Si(001) [15–17].

The measured core-level spectra [4] also indicate O–H cleavage for the adsorption of 2,3-butanediol: The spectra are interpreted in terms of the formation of Si–H and Si–O bonds. Apart from the H dissociation, no further fragmentation of the molecule should occur. Based on this experimental information, we study a number of conceivable bonding sites for the two conformers shown in Fig. 2. We consider positions where butanediol adsorbs on top of one Si dimer (T), bridges the ends of two adjacent dimers within the dimer row (E), and bridges two dimers of neighboring dimer rows (B). The dissociated hydrogen atoms are adsorbed on the adjacent dimer in case (T) or saturate the remaining dimer dangling bonds in the cases (E) and (B). The adsorption energies for these interface geometries are summarized in Table 1 for coverages of 0.25 and 0.5 ML. We find that the top-dimer model (T) with the gauche conformation leads to the