Adsorption of C_2H_2–C_2O_3 on Si(001)

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The adsorption of maleic anhydride on the Si(001) surface was investigated using the first-principles pseudopotential formalism. Our results indicate that C_2H_2-C_2O_3 adsorbs through a [2+2] cycloaddition of the C–C bond to the dangling bonds of Si–Si dimers, as observed for other small hydrocarbons. According to our calculations, the adsorption of a second maleic anhydride molecule will preferentially occur on first-neighbours Si–Si dimer sites in either the dimer chain our dimer row, i.e. considering a (4×2) reconstruction, C_2H_2-C_2O_3 can either form a linear chain or a zig-zag chain, depending on the growth conditions. Although both structures are found to be stable from the energetic point of view, only our STM theoretical images for the linear chain are comparable to available experimental data.

1   Introduction

The increasing relevance of organic films in a great number of technological applications has motivated several investigations of the interaction of organic molecules with semiconductor substrates, specially silicon. It has been recently suggested [1] that the functionality associated with maleic anhydride can be used as controlled bonding sites for linking other organic substituents. Recent experimental investigations by Bitzer and co-workers [1, 2, 3] indicate that, depending on its coverage, C_2H_2=C_2O_3 can adsorb either on inter-dimer sites (or [1+2+1] cycloaddition as in Fig. 1(b)) or through [2+2] cycloaddition (Fig. 1(a)). Our aim in this work is to investigate the adsorption process of maleic anhydride on the silicon surface. For doing so, we employ the state or art pseudopotential method, within a generalized gradient approximation to the density functional theory to investigate different adsorption sites for the maleic anhydride on the silicon surface.

The surface was modelled in a super-cell geometry, with an atomic slab of six Si layers and a vacuum region equivalent to eight atomic layers. On the top side of the slab we placed the C_2H_2=C_2O_3 molecule in different configurations, and the back surface was passivated by H atoms arranged in a dihydride structure. The pseudopotentials for Si, C, O and H were derived by using the scheme of Troullier and Martins [4] and the electron-electron exchange-correlation interactions were considered by using a generalized gradient approximation (GGA) [5] of the density functional theory. The single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 35 Ry. For the Brillouin-zone summation, four special **k** points were used. The atoms were assumed to be in their fully relaxed positions when the forces acting on the ions were smaller than
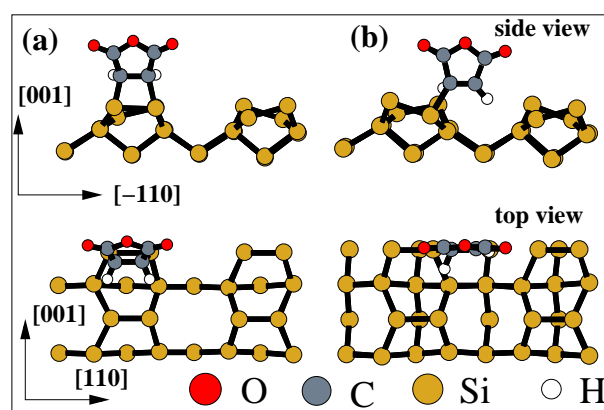
0.005 eV/Å.

Figure 1.   Schematic view of possible adsorption models for C_2H_2=C_2O_3 on Si(001)–(2×4): a) [2+2] cycloaddition, b) inter-dimer.

2   Results

For bulk silicon our first-principles calculations produced 5.50 Å for the equilibrium lattice constant (a_o), 0.86 GPa for the bulk modulus (BM), and 4.39 eV for the cohesive energy, all in good agreement with the the experimental values presented in Ref. [6]. The calculated theoretical lattice constant obtained for the bulk silicon is used in surface calculations. Our calculations support the tilted Si–Si dimer model that characterizes the clean Si(001)–(2×1) surface: the Si–Si dimer is found to have a bond length of 2.30 Å and a vertical buckling of 0.73 Å, indicating a tilt angle of 17.8°. Our calculated bond lengths for the maleic anhydride

molecule are C–C=1.37 Å for the double bond and 1.52 Å for the single bond, C–O=1.37 Å for the double coordinated oxygen and 1.19 Å for the single coordinated one, and C–H=1.10 Å, in good agreement with available experimental data [6].

Our first-principles calculations indicate that, for small coverages (1 molecule per Si–Si dimer, or 0.125 monolayers (ML)) $C_2H_2=C_2O_3$ adsorbs via a [2+2] cycloaddition reaction, via the C=C functionality (Fig. 1(b)), with an adsorption energy of 42 kcal/mol. This is in agreement with the experimental findings of Bitzer and co-workers [2] but is slightly larger than the 31 kcal/mol calculated by Hofer *et al* [7] in a very recent calculation. This difference is probably related to the small size of the cell used in their work. In contrast to the experimental suggestions by Bitzer and co-workers [3], the adsorption on an inter-dimer site (Fig. 1(a)) is found to be energetically unfavourable by almost 30 kcal/mol when compared to the free molecule and the bare Si(001) surface. This is also against the indirect calculations by Hofer *et al* [7] based on elasticity theory. We understand that the main problem in Hofer's calculation is related to the strain energy obtained using a small cell, as this small cell does not take in consideration dimer-dimer interactions, for example.

As the indication of a inter-dimer adsorption was based on STM images [3], we show in Fig. 2 theoretical STM images for both the [2+2] cycloaddition and the inter dimer models. It is worthy pointing out that the present theoretical images are much richer than the experimental ones. If only the brighter spots are considered, our data suggest that it would be very difficult to differentiate between the considered models, as in both cases the adsorbates appear to be dislocated. Therefore we understand that our total energy calculations are consistent with the available experimental STM images.

3 Conclusion

Our total energy calculations suggest that, for low coverages, maleic anhydride adsorbs preferentially via a [2+2] cycloaddition directly over a Si–Si dimer and not in inter dimer sites, as recently suggested by Bitzer and co-workers [3, 7]. Calculated STM images for the both adsorption models are presented and compared to recent experimental observations with a view to support the proposed adsorption model.
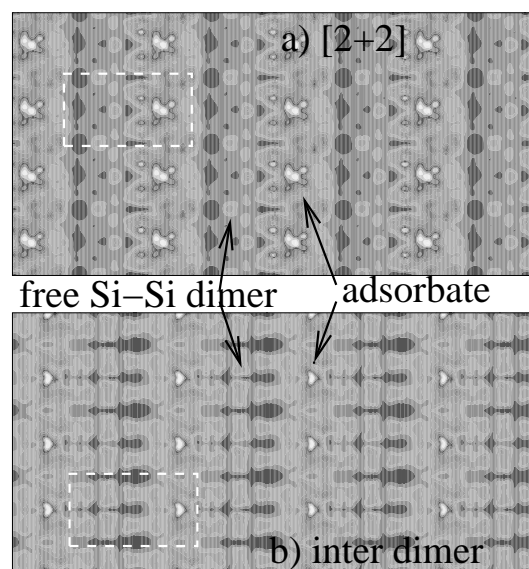

Figure 2. Calculated STM images for occupied states (bias voltage of 2.7 V) for the adsorption of $C_2H_2=C_2O_3$ on Si(001)–(2×4) considering a) [2+2] cycloaddition (0.125 ML) and b) inter-dimer. The dashed rectangle indicates a (4×2) reconstruction.

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