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Chemisorption of Trimesic Acid on a Si(111)-7 × 7 Surface

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Received: October 13, 2009; Revised Manuscript Received: December 21, 2009

Organic nanostructures on semiconductors are currently investigated due to their promising electronic properties. Deposition of trimesic acid molecules was achieved at room temperature on the Si(111)-7 × 7 surface. The adsorbed molecules adopt mainly two different arrangements observed by STM, which have been explained by two cumulative effects: (i) the match of the geometry of the molecule and the surface and (ii) the formation of three covalent bonds by the molecule with silicon adatoms of the surface. The adsorption conformation is presented and discussed by density functional theory calculations and by comparison with experimental STM results.

Introduction

The deposition of molecules on substrates is a topical area of current research in view of their promising electronic properties.^{1,2} In the case of metal substrates, the molecular assembly is controlled by directional intermolecular interactions and tuned by the balance between molecule/molecule and molecule/substrate interactions. In this way, the carboxylic acid derivatives are extensively used to develop supramolecular assemblies on metal surface due to the strong interaction between carboxylic moieties.^{3–12} In the case of semiconductor surfaces, the molecule/substrate interaction is important for the growth of supramolecular self-assemblies.^{13–25} In these cases, carboxylic acid derivatives have been successively used to develop organic networks.^{26–31} Herein, we describe the adsorption of carboxylic acid derivatives, trimesic acid (TMA, 1,3,5-benzenetricarboxylic acid) on a Si(111)-7 × 7 surface at room temperature using scanning tunnelling microscopy (STM). The grafting of molecules on the surface onto specific adsorption sites with OH cleavage bonds is explained by density functional theory (DFT) calculations.

Experimental Methods

STM Experiments. The Si(111)-7 × 7 surface has been chosen because its atomic and electronic structure is well-established. Hence, it is a suitable surface to gain insight into the atomic mechanism of adsorption. Trimesic acid (TMA, 1,3,5-benzenetricarboxylic acid) is a tricarboxylic acid with 3-fold symmetry axis, comprising a central benzene ring and three identical carboxylic end groups in the same plane (distance between carboxylic groups, 0.8 nm). The Si(111) substrate was heated under ultrahigh vacuum by direct current. Clean surfaces were obtained by repeated cycles of heating at 1200 °C and slow cooling to room temperature. Deposition of the molecules from a Mo crucible was performed at 390 K onto the sample maintained at room temperature. All STM experiments were performed with an Omicrometer microscope and were carried out in an ultrahigh vacuum chamber with a pressure lower than 2×10^{-10} mbar. STM images were acquired in the usual constant-current mode at room temperature.

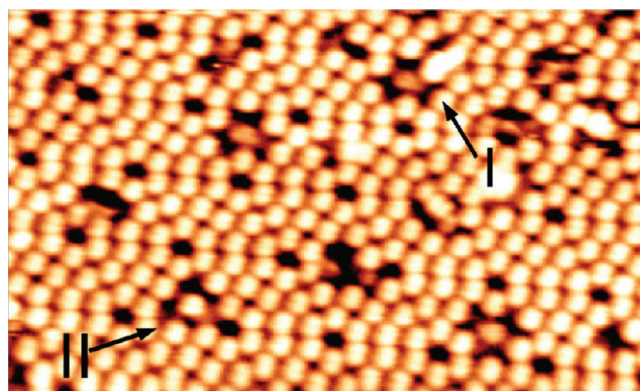


Figure 1. STM image after deposition of TMA molecules on a Si(111)-7 × 7 surface at room temperature ($17.1 \times 10.8 \text{ nm}^2$, $I_t = 0.22 \text{ nA}$, $V_s = +2.13 \text{ V}$).

Results

Figure 1 shows a high-resolution STM image in the empty state of Si(111)-7 × 7 after exposure to TMA molecules (0.14 monolayer of coverage, where one monolayer corresponds to one molecule per half-cell). The clean Si(111)-7 × 7 reconstruction is mainly preserved, even if some defaults are observed. Two types of modified half-cells, including a bright protrusion, named case I and case II, are observed, with more of case I. The bright protrusions are visible on both faulted and unfaulted half-cells. The protrusions do not correspond to Si adatoms, and their apparent diameter is close to 0.7 nm. Protrusions in case II are brighter than in case I.

For case I (Figure 2a), a bright protrusion at the center of the half-cell is observed. The three center adatoms are not visible (white circle), whereas the three corner adatoms are always bright (black circle). For case II (Figure 2b), a bright protrusion above a rest-atom is observed. The corner and the two center adjacent adatoms (white circle) of this rest-atom have disappeared, whereas the three other adatoms are always bright (black circle).

Discussion

As described in the literature, the disappearance of Si adatoms is attributed to the elimination of their dangling bond due to

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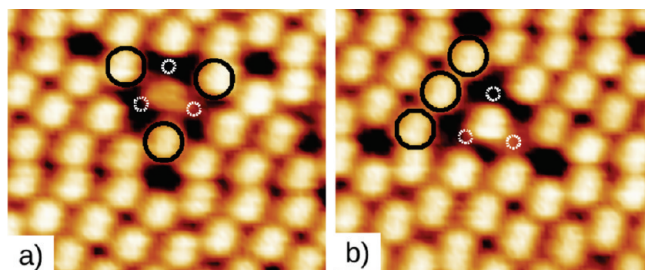


Figure 2. Zoom in (size = 5.2 nm \times 4.3 nm) of Figure 1 showing an individual TMA molecule: (a) centered on the middle of a half-cell, case I; (b) above a rest-atom, case II. The black circles represent bright Si adatoms; white circles, Si adatoms disappeared.

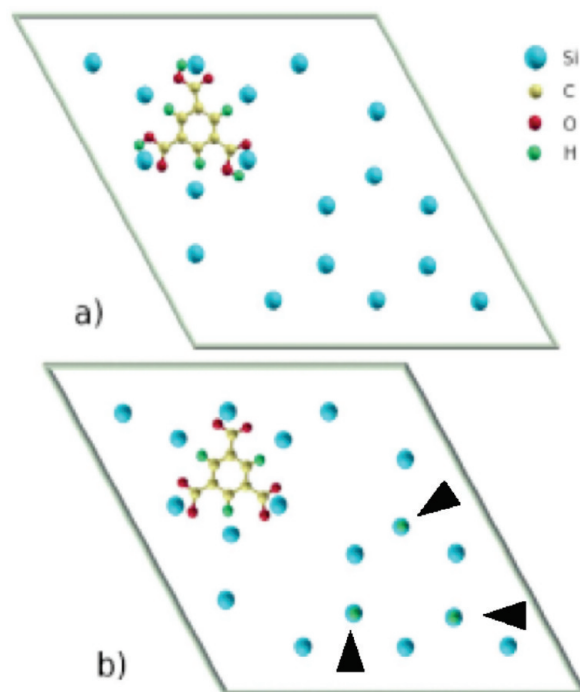


Figure 3. Binding modes of trimesic acid on a simplified Si(111)-7 \times 7 (i.e., 12 adatoms and 6 rest-atoms); top view model corresponds to case I. (a) Nondissociated trimesic acid, case I-ND. (b) Dissociated trimesic acid with three H atoms covalently bonded on Si rest-atoms (black arrows), case I-D.

the formation of a covalent bond with an adsorbate.²⁵ Notwithstanding that, for the interpretation of the experimental results, two possible binding modes of trimesic acid on Si(111)-7 \times 7 can be proposed. The case I-ND (Figure 3a) corresponds to the formation of three bonds between oxygen atoms of carbonyl end groups and the Si center adatoms. The case I-D (Figure 3b) corresponds to the dissociation of the three OH bonds of the TMA. These dissociations induce the chelation of the Si center adatoms by the TMA molecules and the adsorption of three H atoms on Si rest-atoms.^{32–36} The adsorption of nondissociated or dissociated TMA molecules is also possible on a rest-atom, and they correspond to the cases II-ND (Figure 4a) and II-D (Figure 4b), respectively.

To interpret the experimental images and provide further insights into the adsorption, the adsorption energy and the integrated local density of state (LDOS) were calculated by using pseudo potential density functional theory (DFT) calculations with the Vienna ab initio simulation package.^{37,38} Because STM images of TMA molecules absorbed on both faulted and unfaulted half-cells are identical, the calculations were arbitrarily performed only on faulted half-cells.³⁹ The interaction between

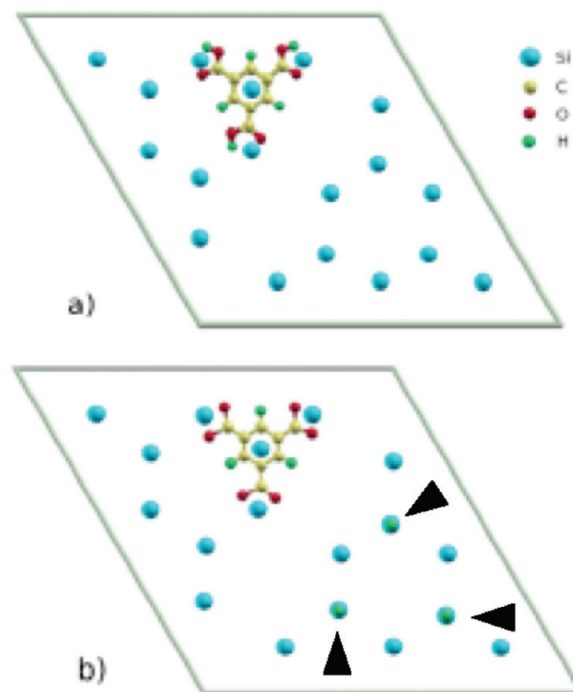


Figure 4. Binding modes of trimesic acid on a simplified Si(111)-7 \times 7 (i.e., 12 adatoms and 6 rest-atoms) top view model corresponding to case I. (a) Nondissociated trimesic acid, case II-ND. (b) Dissociated trimesic acid with three H atoms covalently bonded on Si rest-atoms (black arrows), case II-D.

ions and electrons has been described by the projector augmented wave method. The generalized gradient corrected approximation functional Perdew–Burke–Ernzerhof and a plane wave cutoff of 322.1 eV were used. The Monkhorst–Pack k -point grid was used corresponding to the gamma point in the unit cell, which is a reasonable choice, given the large size of the chosen super cell.

The structure (slab) contained 270 atoms (200 Si, 9 C, 6 O, 55 H) separated by a vacuum spacer to form a periodic computation cell with a 7 \times 7 unit cell of 200 Si atoms and 49 back-face hydrogen atoms. The accepted model for this surface is the dimer–adatom–stacking (DAS) fault model proposed by Takayanagi et al.⁴⁰ It contains 102 Si atoms related at the surface and one bilayer of the bulk Si(111)-1 \times 1 (98 Si atoms). The H atoms were positioned to saturate the silicon dangling bonds at the bottom of the structure.

In all simulations, the positions of all TMA atoms as well as those of whole Si(111)-7 \times 7 were fully optimized using the force and the total-energy minimum RMM-DIIS minimization algorithm until a numerical accuracy less than 1×10^{-3} eV/Å for the total force and an energy variation inferior at 1×10^{-4} eV were reached. For the hypotheses I-D and II-D, the adsorption energy were calculated with the H atoms coming of the OH bond cleavage positioned on rest-atoms of the neighbored unfaulted half-cell to conserve the same atom numbers. Hydrogen atoms are adsorbed preferentially on rest-atom sites rather than adatom sites with a binding-energy difference of around 0.2 eV.⁴¹ Integrated LDOS images were obtained following the Tersoff–Hamann approach, in which constant-current images are approximated by an isosurface of the LDOS, integrated between the Fermi energy (E_f) of the system and the bias voltage (V_s) corresponding to an energy ($E_f + eV_s$).⁴²

The calculated adsorption energy for the four cases I-ND, I-D, II-ND, and II-D are $E_{I-ND} = -2.34$ eV, $E_{I-D} = -6.54$ eV,

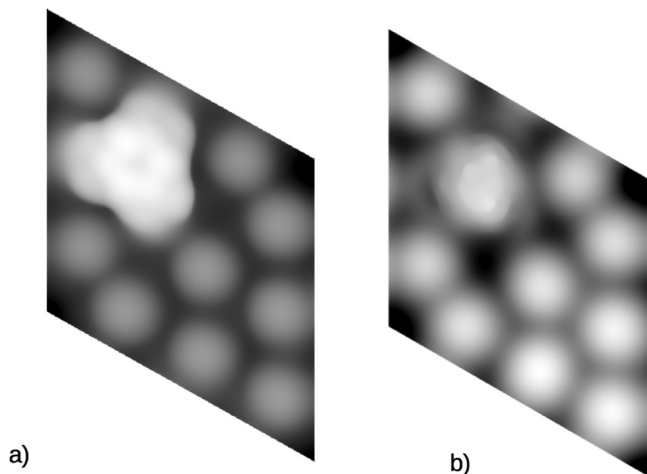


Figure 5. Integrated LDOS of TMA molecules adsorbed on faulted half-cell at $V_s = +2.13$ V in case (a) I-ND and (b) I-D.

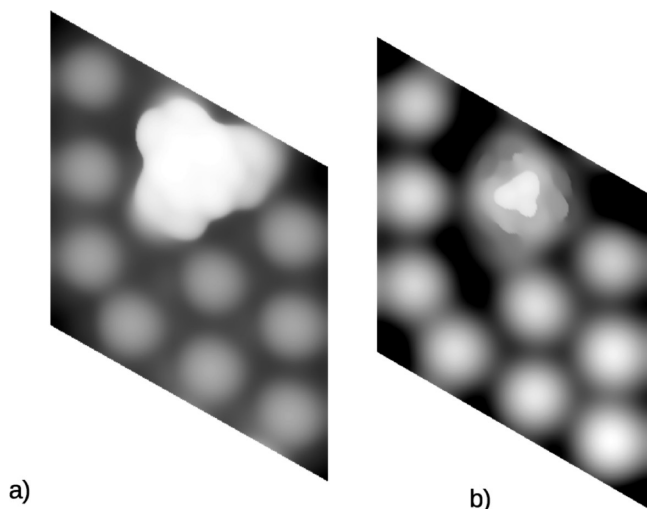


Figure 6. Integrated LDOS of TMA molecules adsorbed on faulted half-cell at $V_s = +2.13$ V case (a) II-ND and (b) II-D.

$E_{\text{II-ND}} = -2.21$ eV, and $E_{\text{II-D}} = -4.54$ eV, respectively. In all cases, the range of calculated energies corresponds to a chemisorption, justifying the choice of DFT to simulate the entire system. The comparison of adsorption energy demonstrates that the adsorption of dissociated TMA molecules is the most favorable on a Si(111)-7 × 7 surface.

Integrated LDOS images were calculated for nondissociated and dissociated TMA molecules corresponding to cases I and II, respectively. For case I-ND, a bright protrusion at the center of the half-cell is observed, and the three moieties are visible (Figure 5a), whereas for case I-D (Figure 5b), a bright central protrusion is still visible, but the three moieties have disappeared in accordance with the experimental STM images (Figure 2a). For case II-ND (Figure 6a), a bright protrusion above a rest-atom is observed, and the three moieties are visible as for the case I-ND. For case II-D (Figure 6b), a bright central protrusion is visible, but one corner and two center adatoms of the half-cell have disappeared, in agreement with the experimental STM images (Figure 2b). In case II-D, the position of the molecule upon a rest-atom creates a central protrusion slightly more intense and less extended (0.78 nm) than for case I-D (0.89 nm).

The integrated LDOS are in good agreement with the experimental STM images, corroborating that the adsorption of TMA molecules on the Si(111)-7 × 7 surface leads to the

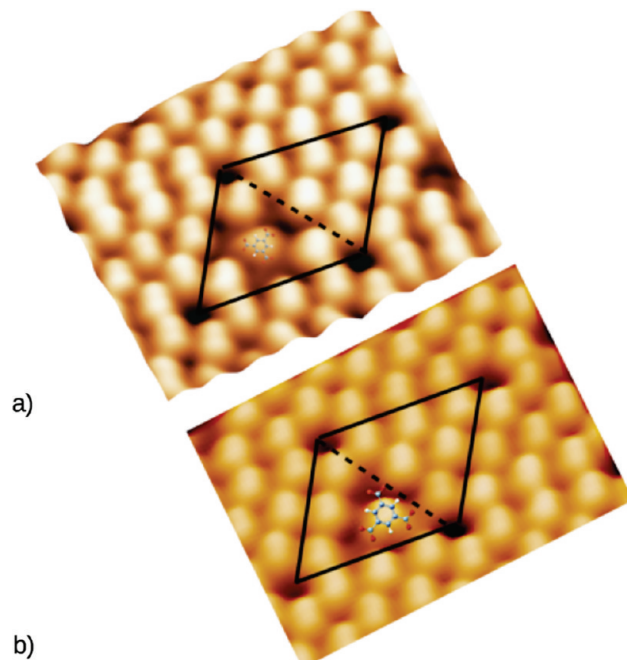


Figure 7. Superimposed ball model of dissociated trimesic acid on an STM image on (a) site I and (b) site II.

dissociation of the O–H bond of TMA molecules. Therefore, on the basis of experimental images and DFT calculations, a model of adsorption of trimesic acid on a Si(111)-7 × 7 surface can be proposed for each site of adsorption as described in Figure 7.

Conclusion

To sum up, the adsorption of trimesic acid on a Si(111)-7 × 7 surface was experimentally and theoretically investigated. Two adsorption sites have been observed, and the chemisorption of TMA molecule via OH cleavage bond was demonstrated by DFT calculations. The covalent anchorage of TMA on the surface via its carboxylic group is prohibitive for the growth of supramolecular self-assemblies. However, the reactivity of TMA versus the Si(111)-7 × 7 surface opens up interesting perspectives to anchor organic molecules on a Si(111)-7 × 7 surface and explore the properties of such hybrid systems for bioengineering and optoelectronics.

Acknowledgment. The authors thank the Communauté d'Agglomération du Pays de Montbéliard, the région de Franche-Comté, and the Agence Nationale de la Recherche (ANR-JCJC-07-0053-01) for their financial support. The authors thank the Institut du Développement et des Ressources en Informatique Scientifique (IDRIS) for allocation of computer time.

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JP909820T