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ABSTRACT

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Adsorption of zwitterionic assemblies on Si(111)-7 × 7: A joint tunneling spectroscopy and ab initio study

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I. INTRODUCTION

The adsorption of functional molecules on solid substrates is vastly becoming a key aspect of nanoscience. To harness the potential of bottom-up strategies, it is essential to grow or manufacture nanostructures in a controlled way. In order to achieve this, a plethora of remarkable architectures has been developed.1–3 Nowadays, the position and the dimension of the molecular assemblies can be tuned and controlled with high precision, i.e., down to the atomic level on metals4–15 or semiconductors.16–27 Yet there are still several challenges in mastering the electronic properties of adsorbed molecular constituents since they can be deeply modified by strong specimen-substrate interactions. Developing technologically robust families of adsorbed assemblies on semiconductor surfaces is challenging, especially because the electronic skeleton of molecules is slightly altered after the adsorption.20,28,29

Despite many attempts, the formation of a nearly complete molecular layer on a semiconductor surface without creating covalent bonds between molecules and substrate is rare, except for the few cases of halogen derivatives adsorption on Si-based surfaces30 or when boron atoms are inserted in the Si(111) surface.31,32 Recently, we have explored an alternative way to realize molecular patterns on Si(111)-7 × 7 thanks to zwitterionic molecules of 4-methoxy-4-(3-sulfonatopropyl) stilbazolium displaying electronic immunity to the chemical reactivity of the crystal.33,34 Unfortunately, while the substrate provided a remarkable template, highly operational hybrid molecular-Si surfaces were not achieved, stemming from the mismatch of the molecule length with the lateral dimension of the Si(111)-7 × 7 half-cell. In order to increase the molecular coverage, a different zwitterionic molecule has been synthesized [4-methoxy-N-(3-sulfonatopropyl) pyridinium (MSP)], closely commensurate with the Si lattice and designed for facilitating rational molecular assembly. By thermal deposition on substrates kept at 340 K, a large-scale patterning of the Si(111)-7 × 7 was observed with MSP molecules arranged perpendicular to the surface.35

Here we report on the adsorption of MSP zwitterionic molecules at low and room temperatures. The interaction between self-assembled zwitterion molecules and the crystal surface has been studied by scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and current image tunneling spectroscopy (CITS). The viable formation of three-zwitterion edifices onto the Si(111)-7 × 7 half-cell is visualized. Furthermore, the experimental results capturing the nanostructuration process and the electronic properties of the molecular constructs are completed by density-functional theory calculations, which give access to the local density of states (LDOS). The good agreement between the simulations and the experimental data suggests a peculiar conformational adsorption of the zwitterionic molecules on the Si(111)-7 × 7 surface.

II. RESULTS AND DISCUSSION

Scanning tunneling microscopy experiments were performed with VT-STM and LT-STM Omicron microscopes in ultrahigh vacuum at a base pressure lower than 2 × 10−10 mbars. The STM images were acquired in constant-current mode at room temperature (RT) and 77 K (see experimental details in Ref. 36). The bias voltage $V_b$ is defined as the sample potential referenced to the tip and was varied typically from −2.2 to 1.9 V. Higher tunneling voltages favor unstable scanning conditions. Normalized STS spectra ($dI/dV$/$dV$) were measured at low temperature through lock-in detection of the ac tunneling current driven by a 7-kHz modulation signal with (10–50)-mV amplitude, added to the junction bias voltage under open-loop conditions. Current image tunneling spectroscopy images were acquired simultaneously with topography maps by positioning the STM tip at every pixel position and then measuring both $I$ vs $V_b$ and $dI/dV$ vs $V_b$. The reported behavior was observed on multiple samples with various tips, which are W or Pt-Ir.

The MSP molecule was synthesized as a model zwitterion, with a sulfonato group ($SO_3^−$) as the anionic site and a...
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FIG. 1. (Color online) (a) MSP Corey-Pauling-Koltun model of the minimum-energy conformation. (b) Chemical structure of the MSP molecule. High-resolution STM images (6.5 × 6.0 nm²) at RT of MSP deposited on Si(111)-7 × 7: (c) filled states (Vₖ = −2.2 V and I = 11 pA) and (d) empty states (Vₖ = 1.9 V and I = 11 pA). (e) Large-scale STM image at 77 K of MSP on Si(111)-7 × 7 (25 × 15 nm², Vₖ = 1.9 V, and I = 100 pA). The disordered appearance of the MSP-decorated surface (with a depth variation of a few atomic layers) differs from the self-organization obtained on large areas by adsorption on substrates kept at 340 K (Ref. 35).

After deposition of the MSP molecules onto the sample at RT, high-resolution STM images of MSP/Si(111)-7 × 7 interfaces were recorded at RT or at 77 K. Scanning tunneling microscopy images recorded with different Vₖ at RT or at 77 K display similar features [see Ref. 36 (SI-2)]. They show preferentially six protuberances observed in the Si(111)-7 × 7 faulted half-cells. High-resolution STM images are detailed in Figs. 1(c) and 1(d); for both filled and empty states, the same half-cell exhibits an original threefold star at the center of images. Three protuberances are situated exactly atop of corner adatoms and the three others are between a rest atom and an adjacent center adatom. In Fig. 1(c), for negative Vₖ, the three protuberances centered on the top of corner adatoms (white circles) are brighter than the three protuberances between a rest atom and an adjacent center adatom (dotted white circles). For positive Vₖ (empty states), the three protuberances between a rest atom and adjacent center adatom are brighter than the same three protuberances observed for the negative bias voltage, as shown in Fig. 1(d). The lateral distance between one corner protuberance and one protuberance between a rest atom and an adjacent center adatom is close to 0.7 nm.

The star shape of the three-member edifices in the Si(111)-7 × 7 half-cells could be attributed to the assembly of three MSP molecules. On the basis of STM experimental images and molecular orbitals of the MSP molecules, we can propose a structural model of MSP molecules adsorbed on Si(111)-7 × 7 half-cells, as shown in Fig. 2. The intense protrusions observed in the filled states atop of corner adatoms are attributed to the sulfonato groups, while the protrusions more intense observed in the empty states between a rest atom and an adjacent center adatom are assigned to the methoxy groups. This empirical model is related to the scheme proposed for the adsorption of 4-methoxy-4-(3-sulfonatopropyl) stilbazolium on Si(111)-7 × 7.33,34 The molecular arrangement of MSP molecules on Si(111)-7 × 7 reveals a chiral character. This is due to the specific locations of the methoxy groups between a rest atom and an adjacent center adatom, leading to a chiral supramolecular arrangement even if MSP molecules are achiral.

After a topological investigation, the electronic structure of MSP molecules deposited on Si(111)-7 × 7 was investigated by CITS. In Fig. 3(a), for negative bias voltage (Vₖ = −1.4 V), the most intense responses are essentially centered atop of protuberances due to the sulfonato groups on corner adatoms [white circles in Figs. 1(c) and 1(d)]. In contrast, as could be seen in Fig. 3(b) for positive bias voltage (Vₖ = 1.6 V), the methoxy groups lying between the corner adatom and the center adatom of the faulted half-cell [dotted white circles in Fig. 1(c)] give the most intense signal. In the combined STM topographic and dI/dV profile images shown in Figs. 3(c) and 3(d), the intensity of the response is correlated with the location of the protuberances of MSP. In Fig. 3(c), the intensity of the response is correlated with the location of the protuberances of MSP. The star shape of the three-member edifices in the Si(111)-7 × 7 half-cells could be attributed to the assembly of three MSP molecules.
MSP unit in the chiral induction of the assemblies mimics the local electronic characteristic. The subtle role of the flexible chirality of the edifices does not translate into a different, are located in a nearly similar chemical environment and the molecule assemblies, we can infer that the MSP molecules band), respectively. By comparing the results for these triple-

[Image 1] (a) High-resolution CITS images (5 × 4 nm²) at 77 K of MSP molecules deposited on Si(111)-7 × 7: (a) filled states (Vᵣ = −1.4 V) and (b) empty states (Vᵣ = 1.6 V). The tunneling resistance was set to 10 G. Maps at Vᵣ = −1.6, −0.9, −0.3, and 1.1 V are available in Ref. 36. (c) High-resolution STM image (5 × 4 nm²) at 77 K showing the chiral assembly of MSP molecules deposited onto Si(111)-7 × 7 (Vᵣ = 0.9 V). The positions of the zwitterions are indicated by dashed yellow lines. (d) Evolution of dI/dV vs Vᵣ along the red line crossing two assemblies of MSP molecules in the topography image (c). (e) Normalized and averaged (N = 6) STS spectra of sulfonato groups of MSP molecules deposited on Si(111)-7 × 7. (f) Normalized and averaged (N = 6) STS spectra of Si corner adatoms without MSP molecules. A noticeable difference is (e) the presence of a local minimum at Vᵣ = 1.1 V for the decorated surface instead of (f) the local maximum detected for the pristine substrate.

III. MODEL SYSTEM AND COMPUTATIONAL METHODS

The simulation of the entire system of molecules and substrate was carried out by the vasp computer program. This method is accurately adapted to interpret the adsorption of molecules on surfaces (see Ref. 36). The MSP molecules were positioned parallel to the Si(111)-7 × 7 surface and two conformational structures were envisioned in order to consolidate the understanding of the STM and CITS images. In Figs. 4(a) and 4(b), MSP molecules are positioned with sulfonato groups on top of the corner adatoms, while in

[Image 2] (Color online) Slab models of the MSP molecules deposited onto Si(111)-7 × 7: (a) top view and (b) lateral view for the model with sulfonato groups on top of the corner adatoms and (c) top view and (d) lateral view for the model with methoxy groups on top of the corner adatoms. The dashed circles highlight the methoxy groups and the black circles correspond to the sulfonato groups.
Figs. 4(c) and 4(d) the MSP molecules are positioned with methoxy groups on top of the corner adatoms. The total energy of these two systems after relaxation is $-1680.98$ and $-1676.25$ eV, which indicates that the conformation with sulfonato groups on top of the corner adatoms, as seen in Figs. 4(a) and 4(b), is the most stable. Most importantly, the results indicate the key role of the atomic scale structure relaxation in the simulated model. The binding energy $E_b$ (see Ref. 36) of three MSP molecules in the optimized conformation with the Si(111)-7 × 7 surface has been computed for the most stable model presented in Figs. 4(a) and 4(b). The binding energy between the molecules and the Si surface is $-1.25$ eV per molecule, which corresponds to an attractive interaction. This calculated adsorption energy for MSP, which prevails on the computed value for the 4-methoxy-4-(3-sulfonatopropyl) stilbazolium of $-0.89$ eV, can be explained by a better match of the molecule length with the lateral dimension of the S(i111)-7 × 7 half-cell. All these data give insight into the possible adsorption model of MSP assemblies on the Si(111)-7 × 7 surface, with the sulfonato group on top of a corner adatom and the methoxy group between a center and rest adatom. Intuitively, the particular screening conditions stemming from the repartition of charge on the Si(111)-7 × 7 surface and on the zwitterionic molecules trigger a slight conformational adaption inducing the three-member star shape ordering of the MSP molecules with a null value for the total dipolar moment in a plane parallel to the surface.

We turn now to LDOS computed images for the model presented in Figs. 4(a) and 4(b). For both negative and positive $V_s$, we observe two protuberances for each zwitterionic molecule (Fig. 5). In the case of negative $V_s$, the three protuberances centered on the top of corner adatoms are brighter than the three protuberances between a rest atom and an adjacent center adatom. In the filled states, the LDOS intensity is proportional to the electronic charge, which is essentially delocalized on the sulfonato groups as can be seen in Figs. 5(a) and 5(c). For positive $V_s$, the LDOS intensity appears to be dominated by the contribution of the empty states, which are partly localized on the pyridinium-methoxy group of the MSP molecules [Figs. 5(b) and 5(d)]. Hence the integrated LDOS images succeed in reproducing well the aforementioned experimental STM and CITS observations reported in Figs. 1 and 3. Simulations and experimental data are in good agreement and support the proposed model for MSP adsorption on a Si(111)-7 × 7 surface. However, in order to definitively prove this model, established surface techniques offer further opportunities for reaching a more detailed picture of the interface structure provided zwitterionic assemblies are sufficiently abundant to yield a signal.

**IV. CONCLUSION**

In summary, the viable adsorption of MSP molecules onto Si(111)-7 × 7 was achieved at room temperature and studied by CITS measurements at 77 K. The adsorption site and conformational adaptation of the molecule on the substrate is fully explained by simulations with a binding energy of $-1.25$ eV per molecule. Scanning tunneling microscopy images, STS spectra, and density-functional-theory calculations enable us to propose an adsorption model of MSP chiral assembly on Si(111)-7 × 7 substrates. Thanks to the adjustment of the molecule zwitterionic length, one can therefore obtain organized nanostructures in a controlled way on Si(111)-7 × 7 surfaces.

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