Selective Attachment of 1,4-Benzenedimethanethiol on the Copper Mediated Si(111)−(7 × 7) Surface through S−Cu Linkage

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The well-defined and patterned copper clusters formed on the Si(111)−(7 × 7) surface have been employed as a template for selective binding of 1,4-benzenedimethanethiol ($HS−CH_2−C_6H_4−CH_2−SH$, 1,4-BDMT), to form ordered molecular nanostructures. Scanning tunneling microscopic (STM) studies showed that each 1,4-BDMT molecule preferentially binds to two neighboring copper atoms within one copper cluster through the S−Cu interaction with its molecular plane parallel to the surface, whereas some 1,4-BDMT bond to individually adsorbed copper atoms, resulting in an upright configuration. Large-scale two-dimensional molecular nanostructures can be obtained using this patterned assembly technique. Our experiments demonstrate the feasibility for controllable growth of ordered molecular nanostructures on the Si(111)−(7 × 7) surface.

To design and build electronic devices based on the properties of single molecules is an important and challenging field of research.[1−3] The covalent binding of organic molecules on semiconductor surfaces has recently received much attention due to its potential applications in molecular electronics.[4−6] Its feasibility was clearly demonstrated in recent experimental and theoretical investigations.[7,8] On the other hand, to reliably wire molecules onto electrodes molecules end-capped with thiol groups can be employed to form covalent bonds with metal surfaces. These include molecules based on conjugated aryl oligomers, such as oligophenyldithiols and oligophenylene−ethynylenedithiols.[9−14] The simple members of this group, benzenedithiol and benzenedimethanethiol, have been investigated experimentally using scanning tunneling microscopy (STM).[11,12] Their small highest occupied molecular orbital (HOMO)−lowest unoccupied (LU)MO gap and the possibility of functionalizing these molecules make them attractive for potential molecular electronic devices.

To fabricate applicable chips of molecular electronics, achieving the desired patterns of molecular arrays and nanostructures is essential and important. One approach is to employ self-assembled systems as templates to create desired nanostructures.[15−17] Ordered semiconductor and metal nanostructure arrays can be formed on the Si(111)−(7 × 7) surface.[18−20] In particular, we showed the self-assembled growth of two-dimensional copper clusters consisting of six Cu atoms on the faulted halves of Si(111)−(7 × 7).[20] On this surface, the molecular reactivity is expected to be significantly different between the two halves of the (7 × 7) unit cell considering the chemical nature of the copper cluster in the faulted half and the free silicon dangling bonds in the unfaulted half. In this letter, we explore the possibility of using the Cu/Si(111)−(7 × 7) surface as a tempting template for selective attachment of 1,4-benzenedimethanethiol (1,4-BDMT), so as to provide a pathway for the formation of ordered two-dimensional molecular nanostructures on the Si(111) surface.

Our experiments were performed using an Omicron variable temperature STM operated in an ultrahigh-vacuum (UHV) chamber (with a base pressure better than $1 × 10^{−10}$ Torr). The sample used in our experiments was cut from a P-doped mirror-polished Si(111) wafer with a resistivity of 1−2 Ω·cm and a size of 12 mm × 2 mm × 0.5 mm. Atomically clean Si(111)−(7 × 7) surfaces were prepared in situ by flashing the sample to 1200 °C after outgassing at 600 °C for 12 h. Copper was deposited onto the surface by resistive heating of a Cu-covered W wire. A typical deposition rate of about 0.1 monolayer (ML)/min was routinely achieved. In this paper, one monolayer coverage of Cu is referenced to the number of surface Si atoms of an unreconstructed Si(111) surface (1 ML = $7.8 × 10^{14}$ atoms/cm²). For STM studies, an electrochemically etched tungsten tip cleaned by in situ heating was employed. All our STM images were acquired in a constant-current mode at room temperature with a tunneling current of 0.1 nA.

1,4-BDMT (99.8%, Aldrich Chemical) was further purified through at least five freeze−pump−thaw cycles before being dosed onto the Si(111)−(7 × 7) surface at room temperature. Dosing was performed through a tube located a few centimeters from the surface, and the exposures were reported in langmuirs (1 L = $10^{−6}$ Torr·s).

The (111) facet of silicon, upon cleaning and annealing, spontaneously reconstructs to a (7 × 7) structure (Figure 1), which can be described by the dimer-adatom-stacking fault (DAS) model.[21] A (7 × 7) structure unit cell has two triangular subunits (faulted and unfaulted) surrounded by nine silicon dimers and contains nineteen dangling bonds associated with twelve adatoms, six rest atoms, and one corner hole. Chemical reactions are most likely to take place at these dangling bonds

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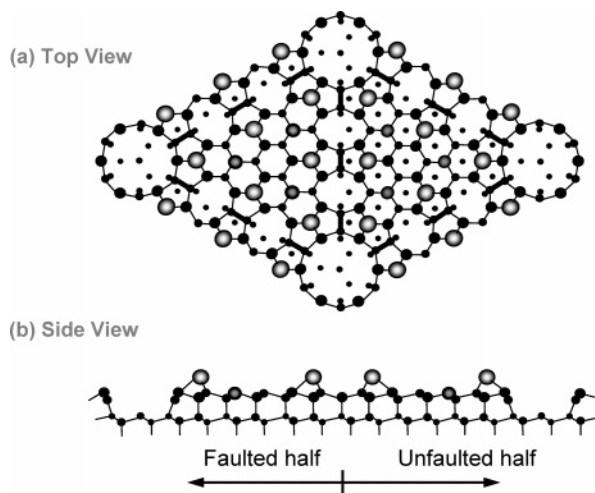† Department of Chemistry.
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Figure 1. Top view (a) and side view (b) of the detailed structure of a Si(111)−(7 × 7) unit cell based on the dimer-adatom-stacking fault (DAS) model proposed by Takayanagi et al. (ref 21). Only adatoms, rest atoms, and corner hole atoms have dangling bonds. Faulted and unfaulted halves of the (7 × 7) unit cell are also marked.

because of their unsaturated nature. The conductance is higher in the faulted half compared to the unfaulted half. Within each half, the electron density on the three corner adatoms is greater than that on the center adatoms. The faulted and unfaulted halves of the (7 × 7) unit cell are also shown in Figure 1.

The formation of ordered metal and semiconductor nano-structures on the Si(111)−(7 × 7) surface is considered to be mediated by the greater attractive potential well existing on the faulted half of the unit cell, which effectively traps adsorbed atoms to create ordered nanostructures with a well-defined size. Figure 2 shows the STM images of copper clusters formed on Si(111)−(7 × 7) at different coverages. At a coverage of 0.02 ML (Figure 2a), the surface is mainly covered by individually adsorbed copper atoms (labeled by white arrows) atop silicon adatom positions with a few copper clusters (black arrows) on the faulted halves of the Si(111)−(7 × 7) surface. As the copper coverage increases to 0.1 ML, the ordered copper clusters (black arrows) become the major feature, as shown in Figure 2b. The number of individually adsorbed Cu atoms is dramatically reduced, although still noticeable. Copper atoms may initially bind to silicon adatoms. Further deposition results in Cu adsorption at silicon rest atom positions to form homogeneous copper clusters. The copper atoms in a cluster interact with each other through the silicon atoms to stabilize the cluster structure, consistent with the fact that individual Cu atoms within one cluster are not readily resolvable in the STM image. These two different types of copper structures on the Si(111)−(7 × 7) surface, homogeneous clusters (type A) and individual atoms (type B), are schematically illustrated in Figure 2c. Details of the formation of copper clusters and its atomic structure can be found in ref 20. The chemical difference between the Cu clusters on the faulted halves and the Si dangling bonds on the unfaulted halves may allow us to achieve molecular patterning within one unit cell.

Figure 3a shows the large-scale STM image of 1,4-BDMT molecular nanostructures formed by exposing the copper prepatterned Si(111)−(7 × 7) surface to 0.8 L of 1,4-BDMT vapor at room temperature. It is readily noticed that the surface is uniformly decorated by regular arrays of two-dimensional triangular nanostructures, which almost exclusively cover the faulted halves of the (7 × 7) unit cells. The actual coverage of the molecules is estimated to be about 0.06 ML. This STM result
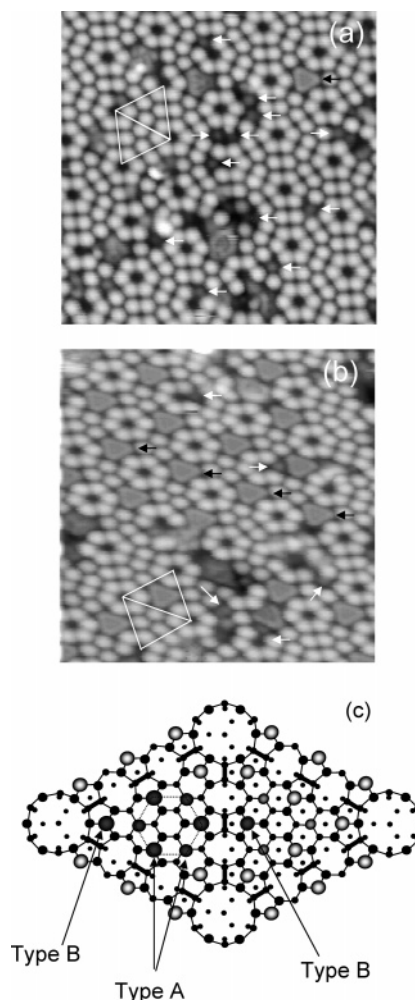

Figure 2. Empty-state STM images of copper deposited on Si(111)−(7 × 7) surfaces at room temperature at coverages of 0.02 ML (a) and 0.1 ML (b). The images were obtained at sample bias voltage of +0.5 V and tunneling current of 0.1 nA with a scan area of 15 nm × 15 nm. The white diamond shape marks a single (7 × 7) unit cell. The STM images reveal two types of copper configurations: type A representing the ordered copper clusters (labeled by black arrows) and type B single copper atoms at corner and center adatom positions (white arrows). (c) Model for copper clusters and single copper atoms on a (7 × 7) unit cell.

clearly demonstrates that 1,4-BDMT molecules are selectively bonded to the Cu clusters on the faulted halves of the Si(111)−(7 × 7) surface instead of the clean unfaulted sides, which is further confirmed by the high-resolution STM image as shown in Figure 3b. Every molecular nanostructure has three bright dots, which may be attributable to three 1,4-BDMT molecules bonded to a copper cluster. The unfaulted half of the Si(111)−(7 × 7) surface, however, remains unreacted.

This high selectivity of 1,4-BDMT binding to copper clusters enables us to fabricate the two-dimensional molecular nano-structures with well-defined size and position. The height profile along line AA′ is shown in Figure 3c. It clearly shows that these molecular nanostructures are evenly distributed on the surface with a uniform size. Besides these ordered molecular nano-structures (labeled by black arrows), there are some very bright dots at adatom positions (labeled by white arrows). These two types of features suggest the existence of two different molecular configurations for 1,4-BDMT bonded to the surface. Type A represents three 1,4-BDMT molecules binding to one copper cluster through S−Cu linkages, whereas type B represents one molecule bonding to a single copper atom in an upright
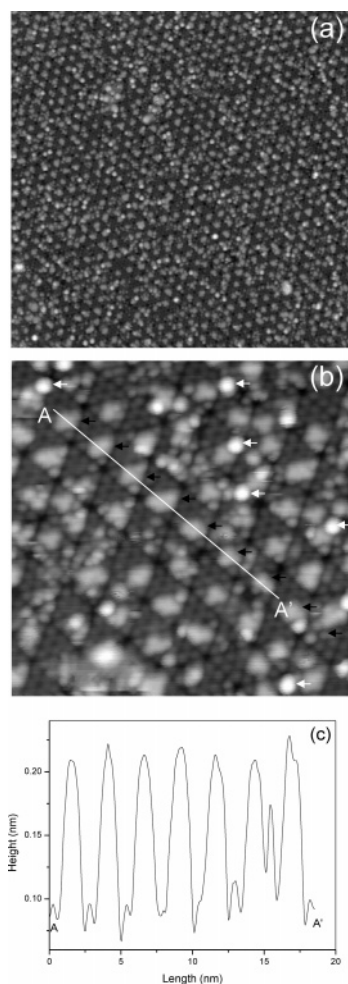
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Figure 3. (a) Large-scale STM image (78 nm × 78 nm) of 1,4-BDMT molecular nanostructures formed on the copper-patterned Si(111)−(7 × 7) surface at sample bias voltage of −2.5 V. The exposure is 0.8 L. (b) High-resolution STM image (25 nm × 25 nm) at sample bias of −2.5 V reveals two types of molecular configurations: type A representing molecules bonded to copper clusters (labeled by black arrows) and type B molecules bonded to single copper atoms at corner and center adatom positions (white arrows). (c) Height profile along the line AA′ labeled in image (b).

configuration. These two binding configurations are schematically illustrated in Figure 4a.

1,4-BDMT adsorbs dissociatively on silver and gold surfaces, resulting in thiolate structures.[22−24] The molecule lies flat on silver because of the loss of both thiol protons, and it stands perpendicularly on the gold surface through one S−Au linkage formed in the reaction of one terminal S−H with the surface. It is well-established that long-chain alkanethiols adsorb on copper, silver, and gold surfaces and form oriented and ordered monolayers.[25−27] Copper surfaces were found to be more reactive than Au or Ag and may facilitate the partial scission of the C−S bond to form sulfur and alkyl species on the surface.[28−30] The copper atoms on the Si(111)−(7 × 7) surface in our case are expected to have a different reactivity compared to the copper surfaces because of the large differences in their atomic structures and electronic properties. 1,4-BDMT may adsorb onto the individual copper atoms through the formation of a S−Cu bond, similar to that of 1,4-BDMT binding to gold surfaces. These adsorbed molecules are expected to be in an upright geometry, and the schematic binding structure is illustrated as type B in Figure 4b. Therefore, the bright dots are a result of the upright configuration, thiol group, and
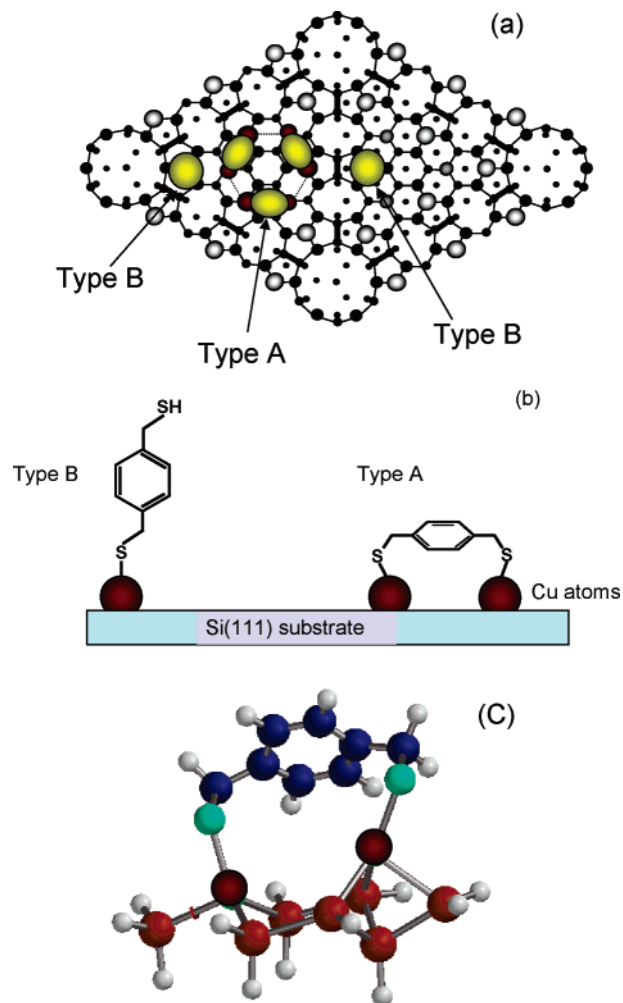
Figure 4. Schematic illustration of the (a) top view and (b) side view of possible configurations of 1,4-BDMT molecules bonded on copper cluster and copper single atoms on the Si(111)−(7 × 7) surface. (c) Scheme of 1,4-BDMT binding to two copper atoms atop neighboring adatom and rest atom in a copper cluster in Type A configuration.

conjugated benzene ring. To understand the possible binding nature of 1,4-BDMT with copper clusters, we need to consider the cluster structure. Each copper cluster consists of three Cu atoms atop Si adatoms and another three on rest atoms. 1,4-BDMT may possibly bond to a pair of neighboring copper atoms at the adatom and rest atom positions. Thus, one copper cluster can accommodate three 1,4-BDMT molecules, and the schematic structure of such a binding configuration is shown as type A in Figure 4b. Figure 4c shows the binding configuration of 1,4-BDMT bonded to copper clusters. The distance of neighboring copper atoms at adatom and rest atom position is 0.456 nm, while the distance of two sulfur atoms in binding state is 0.535 nm. Thus, it is reasonable to propose 1,4-BDMT bonded to two copper atoms in a cluster in geometric consideration. Further experimental studies are certainly required to confirm the chemical structures of these binding modes.

In summary, using ordered copper clusters as a prepatterned template, we have studied the selective attachment of 1,4-BDMT on the Cu-covered Si(111)−(7 × 7) surface. The 1,4-BDMT molecules were found to either bind with two copper atoms within a copper cluster through the S−Cu interaction or on individual copper atoms in an upright configuration. This prepatterned assembly technique may possibly be employed to form a variety of molecular nanostructures on the Si(111)−(7 × 7) surface.

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