Mechanism for Room-Temperature Single-Atom Lateral Manipulations on Semiconductors Using Atomic Force Microscopy

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Since the first demonstration of atom-by-atom assembly, well-controlled lateral manipulations using scanning tunneling microscopy (STM) have provided a fascinating tool for stunning realizations in nanoscale science. In most of those experiments, atoms and molecules were individually dragged over the surface upon an enough tip vertical proximity. To do so, the thermal and mechanical stability provided by a cryogenic environment was a requirement. Recently, a new exciting panorama has been opened with the ability of atomic force microscopy (AFM) to atom-by-atom manipulations with sophisticated nanostructuring at semiconductor surfaces under room temperature conditions. To shed some light on the detailed mechanism behind these novel room temperature manipulations on semiconductors using AFM, we clarified the mechanism for the lateral manipulation of intrinsic adatoms of the Si(111)-(7x7) surface in the presence of a single atomic vacancy at room temperature. By combining experiments and first-principles calculations, we showed that, for the measured attractive short-range forces associated with the manipulation set point, the presence of the semiconductor tip lowers, very locally, the energy barriers for the adatoms' natural diffusion near the limit that enables the thermally activated hopping between adjacent adsorption sites.

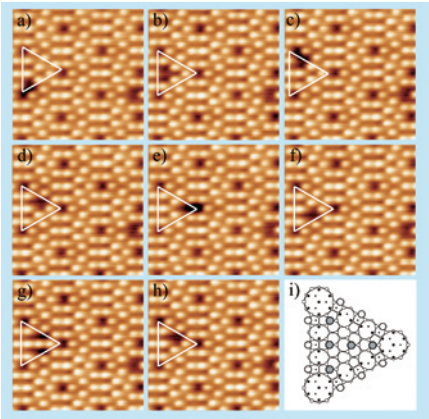

Fig. 1 Topographic images, (a) to (h), from a series of vacancy-mediated manipulations of intrinsic adatoms of the Si(111)-(7×7) surface. Si adatoms in the white triangles were successively manipulated, as a result, a vacancy position was changed. In (i), a model of the atomic configuration for the highlighted unit cell in (g), which we found in this study, is displayed.

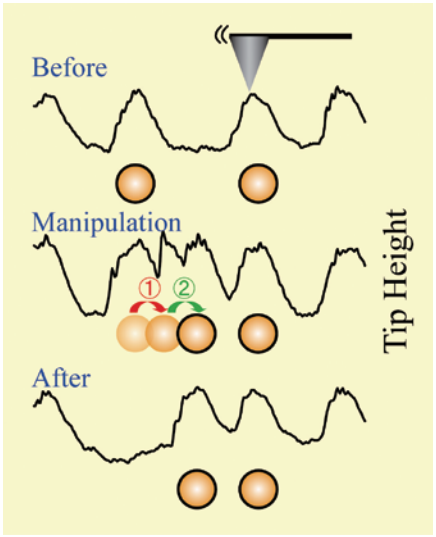

Fig. 2 The tip trajectory of before, during, and after manipulation. During the topographic tip scanning for manipulation, a Si atom changed the adsorption positions twice. In this experiment, the signature of the lateral atom manipulation using AFM was observed for the first time.

Site-Selective Guest Inclusion in Molecular Networks of Butadiyne-Bridged Pyridino and Benzeno Square Macrocycles on a Surface

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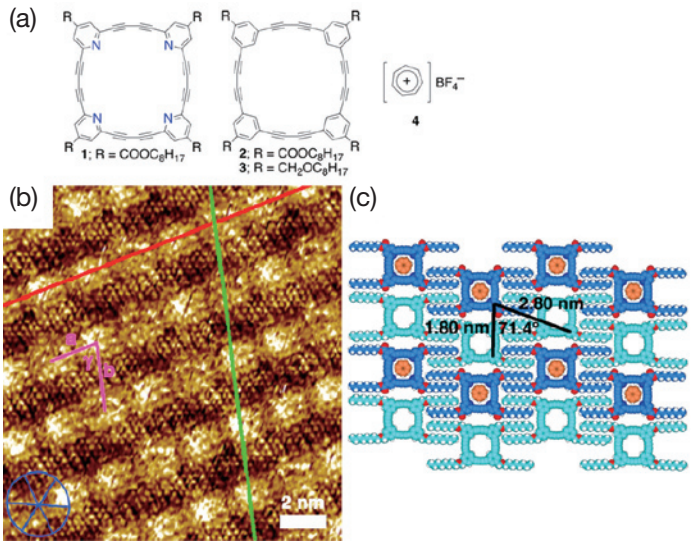

Fig. 1. (a) Chemical structures of macrocycle **1**-**3** and Tr cation **4**. (b) An STM image of modular network. (c) Tentative network model.

Alignment of functional molecules on two-dimensional (2D) molecular networks on solid surfaces is of current interest owing to potential nanotechnological applications, such as the fabrication of molecular scale devices and machines. Recently, multi-component networks formed by directional intermolecular interactions or by 2D host-guest chemistry involving a molecular network have received considerable attention. We present the first observation of modular molecular networks formed by two different types of square-shaped "host" molecules and site-selective "guest" inclusion.

Butadiyne-bridged planar macrocycles **1–3** are chosen as host molecules because of the anticipated formation of a regular porous network (Figure 1a). Moreover, pyridinophane **1** shows a high binding affinity to tropylium (Tr) cation **4** via ion-dipole interactions. With these components in hand, we examined the formation of modular networks formed by a mixture of macrocycles - **1**/**2**, **1**/**3**, or **2**/**3** - having different side chains and site-selective guest binding properties, by using the **4** as molecular marker.

Figure 1b shows the modular molecular network formed by applying a mixture of **1**, **3**, and **4** in a 1:1:13 molar ratio in TCB/CH_3CN/$CHCl_3$ (20/9/1) on the graphite surface. The structural feature of the modular network is different from that formed by each macrocycle. The network model is shown in Figure 1c. The stripe features are adsorbed alkyl chains, relatively bright features correspond to the π-core of **1**+**4** complex, and the other parts are the π-core of **3**. Careful analysis of positional relationships between macrocycles reveals a clear tendency of **1**+**4** complex and **3** to appear in an alternating fashion along unit cell vector *a* (the red line in Figure 1b). Based on the facts that a mixture of **2** and **3** also forms this modular network and a mixture of **1**, **2**, and **4** does not show modular network, the driving force for this preferred alternation along only one direction is attributed to attractive dipolar interactions between adjacent ester and ether groups of the side chains along the macrocycle rows (unit cell vector *a*).

We believe the modular network approach presented here can lead to a general strategy for the construction of multi-component 2D molecular networks in which different kinds of molecules are aligned on the surface in a site- and space-defined manner.