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Theoretical Prediction of Heterogeneous Molecular Wires on the Si(001) Surface

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Fabrication of hybrid organic molecular silicon surfaces has been a fascinating subject because of its potential application for new sensor and molecular device technologies.[1,2] Recently, a variant of the hydrogen resist scanning tunneling microscope nanolithography technique, termed feedback controlled lithography (FCL),[3−5] was used to generate arbitrary arrays of individual dangling bonds on the Si(001) surface. The surface is then dosed with appropriately chosen organic molecules that will bind only at the patterned dangling-bond sites. Using this self-assembly technique, organic molecules, such as norbornadiene[6] and 2,2,6,6-tetramethyl-1-piperidinyloxy,[7] have been anchored to silicon dangling-bond arrays.

In the present work, we theoretically predict that the above self-assembly technique can be extended to the construction of one-dimensional (1D) heterogeneous molecular wires composed of two different organic molecules. Using the FCL, the dangling-bond (DB) wire can be generated by the selective removal of H atoms from a H-passivated Si(001) surface along the Si dimer row (see Figure 1a).[3,8] This DB wire is composed of the alternating up and down Si atoms which are negatively and positively charged, respectively.[8] Hence, the electron-abundant up (electron-deficient down) Si atom is expected to be easily reactive with the Lewis acid (base) molecule, resulting in the formation of a covalent bond. Using such different selective adsorptions of Lewis acid and base molecules on the DB wire, we propose a way for constructing a heterogeneous molecular wire where pyridine (base) and borine (acid) molecules adsorb alternatively along the DB wire. Such a self-assembly technique for formation of the heterogeneous molecular wire can be generally applicable to other pairs of Lewis base and acid molecules.

First, we consider the interaction of pyridine with the DB wire generated on an H-passivated Si(001) surface. Since pyridine contains a single N lone pair, the N atom will be easily attracted to the electrophilic down Si atom in the DB wire, forming a dative N−Si bond. Recent experimental studies for the adsorption of ammonia,[9] trimethylamine,[10] and pyridine[11] on Si(001) or Ge(001) observed such a selective bonding with the down atom of the Si or Ge dimer. Using first-principles density-functional theory calculations,[12] we optimize the structure of the “down-site” pyridine wire (see Figure 1b) where pyridine molecules are attached to all the down Si atoms in the DB wire. Here, the surface was modeled by a periodic slab geometry containing six Si atomic layers. The bottom Si layer of the slab is passivated by two H atoms per Si atom. Further details of our calculational scheme are given in the Supporting Information. We find that the down-site pyridine wire has an adsorption energy (E_{ads}) of 1.29 eV. As the counterpart of the down-site pyridine wire, we also optimize the structure of the “up-site” pyridine wire where pyridine molecules are attached to all the up Si atoms. However, the up-site pyridine wire is found not to be stabilized. This may be due to a strong repulsion between the lone pair of the N atom and the occupied dangling bond of the up Si atom. Thus, we can say that pyridine adsorption on the DB wire will occur selectively at the down Si atom site, thereby forming a self-assembled down-site pyridine wire.

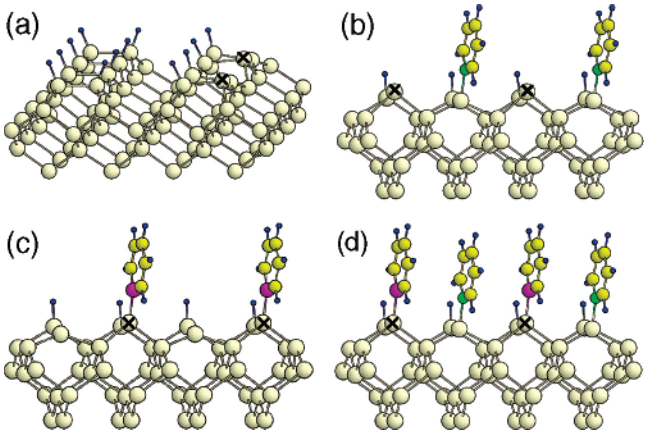

Figure 1. Perspective and side views of the optimized structures of (a) the DB wire on a H-passivated Si(001) surface, (b) the down-site pyridine wire, (c) the up-site borine wire, and (d) the pyridine−borine wire. The circles represent Si, B, C, N, and H atoms with decreasing size. For distinction, the up Si atoms in the DB wire are marked (X).

Parallel to the case of pyridine wires, we consider the up-site and down-site borine wires on the DB wire. Contrasting with pyridine adsorption, which involves a dative N−Si bond formed by sharing the N lone-pair electrons, borine adsorption may form a dative B−Si bond by a charge donation from the electron-abundant up Si atom. In Figure 1c, we display the optimized structure of the up-site borine wire which has $E_{\mathrm{ads}} = 1.68$ eV (see Table 1). Interestingly, our calculation for the down-site borine wire shows that during structure optimization the buckling configuration of the up and down Si atoms is switched; that is, the initially taken down-site borine wire converges to the optimized structure of the up-site borine wire (but shifted by half unit-cell length along the dimer row). This result indicates that unlike pyridine adsorption the adsorption site of borine is not selectively determined, implying that the bonding nature of the Si−B bond in the borine wire should differ from that of the Si−N bond in the pyridine wire.

To examine the difference in the bonding nature between the pyridine and borine wires, we plot the charge densities ($\rho_{\mathrm{molecule/Si}}$) of adsorbed pyridine and borine in Figure 2a and 2b, respectively. Compared with the charge densities of the isolated pyridine and borine wires (see the insets in Figure 2a and 2b), it can be seen that upon borine adsorption a significant change of electron charge occurs around the B atom. The calculated charge density difference, defined as

$$\Delta\rho = \rho_{\mathrm{molecule/Si}} - (\rho_{\mathrm{molecule}} + \rho_{\mathrm{Si}}) \qquad (1)$$

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Table 1. Calculated Adsorption Energy of Various Pyridine and Borine Wires Coupled with the DB Wire on Si(001)

structure	E_{ads} (eV)
down-site pyridine wire	1.29
up-site borine wire	1.68
borine wire (full-coverage)	1.80
pyridine−borine wire (full-coverage)	3.57[a]

[a] Adsorption energy per a pair of pyridine and borine molecules.

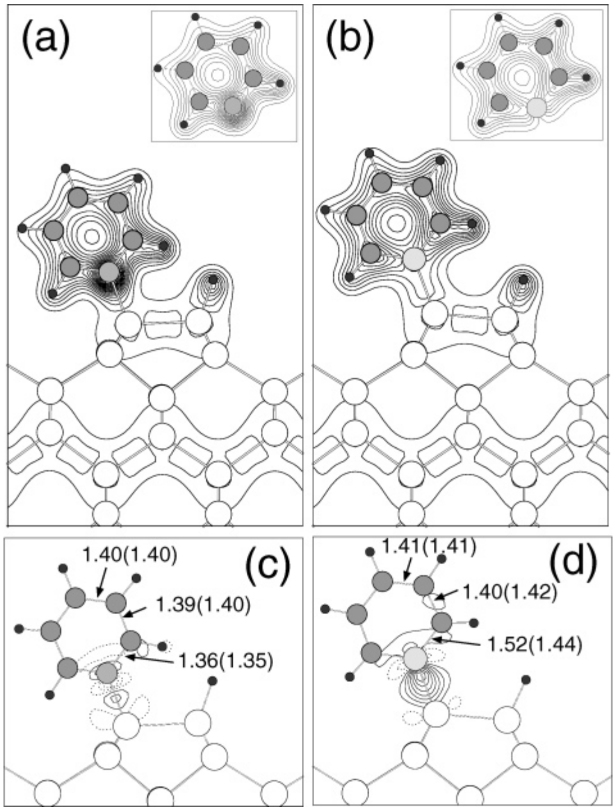

Figure 2. Calculated charge densities for adsorbed (a) pyridine and (b) borine in the down-site pyridine and the up-site borine wires. The charge density differences, defined in eq 1, in the down-site pyridine and the up-site borine wires are given in (c) and (d), respectively. In (a) and (b), the contour spacing is 0.03 e/bohr^3. The charge densities of pyridine and borine in the isolated pyridine and borine wires are also given in the insets of (a) and (b), respectively. In (c) and (d), the contour spacing of the solid (dashed) line is 0.01 e/bohr^3 (-0.01 e/bohr^3). The numbers denote the bond lengths in Å. For comparison, the bond lengths of a free molecule are given in parentheses.

clearly shows that electron charge is more dominantly redistributed in adsorbed borine compared to that in adsorbed pyridine (see Figure 2c and d). Here, ρ_{molecule} and ρ_{Si} are the charge densities of the separated systems, that is, the isolated molecular wire and the Si substrate, respectively. This result demonstrates that pyridine adsorption involves a dative bonding with marginal charge redistribution, but borine adsorption accompanies significant charge redistribution along the B−Si bond. Such a different bonding nature of the two systems is well represented by the calculated bond lengths of molecules. As shown in Figure 2c and 2d, the bond lengths of adsorbed pyridine are almost the same as those of a free pyridine molecule, while upon adsorption, the bond lengths ($d_{\mathrm{B-C}}$) between the B atom and its bonding C atoms largely increase by 0.08 Å. This increase of $d_{\mathrm{B-C}}$ in adsorbed borine together with a significant accumulation of electron charge along the B−Si bond manifests the bond reordering between the B atom and its bonding elements, such as the two C atoms and the Si atom.

On the basis of our findings, we propose how to fabricate a heterogeneous molecular wire composed of alternating pyridine and borine molecules on the DB wire. It is necessary that the DB wire is initially exposed to dose of pyridine under ultrahigh vacuum conditions, forming the down-site pyridine wire. Subsequently, borine dosing on the self-assembled down-site pyridine wire will lead to formation of the heterogeneous pyridine−borine wire (Figure 1d) on the DB wire. We find that this pyridine−borine wire has an adsorption energy of 3.57 eV (per a pair of pyridine and borine molecules), larger than the sum of adsorption energies of the down-site pyridine wire ($E_{\mathrm{ads}} = 1.29$ eV) and the up-site borine wire ($E_{\mathrm{ads}} = 1.68$ eV), implying a strong attractive intermolecular interaction mediated by the surface.[13] Although we do not study the adsorption kinetics in the present study, the reaction of borine with a Si dangling bond after the formation of the down-site pyridine wire is likely to be more facile than that on the bare DB wire because of the greater enhancement of adsorption energy in the former case compared to that in the latter one. It is notable that, if the DB wire is initially exposed to borine vapor, borine will be attached to all the up and down Si atoms because borine can interact with both Si atoms. Such a full-coverage borine wire also has a larger adsorption energy of $E_{\mathrm{ads}} = 1.80$ eV compared to that ($E_{\mathrm{ads}} = 1.68$ eV) of the up-site borine wire.

In summary, we theoretically propose a self-assembly technique for fabrication of the heterogeneous pyridine−borine wire on the DB wire generated on a H-passivated Si(001) surface. Our first-principles density-functional calculations suggest that pyridine, which selectively bonds to the down Si atom, is needed to dose the DB wire before borine dosing, resulting in formation of the pyridine−borine wire. This procedure may be extended to other pairs of Lewis base and acid molecules. We hope that our predictions will stimulate experimental works for fabrication of various heterogeneous molecular wires coupled with the DB wire on the Si(001) surface. Further investigations on the electronic properties of various heterogeneous molecular wires will be of interest both theoretically and experimentally.

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Supporting Information Available: Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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