Theoretical prediction of 1-D molecular lines on the Si(001) surface

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Theoretical Prediction of 1-D Molecular Lines on the Si(001) Surface

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Abstract. We propose a facile method for the self-directed growth of 1D molecular lines on the H-terminated Si(001) surface. This method employing a single H-free dimer instead of a single DB greatly enhances the stability of the radical intermediate, thereby facilitating the chain reaction for 1D molecular lines. The proposed method will stimulate experiments for fabrication of 1D molecular lines which are strongly attached to the Si(001) substrate.

1. Introduction

Self-assembly of organic nanostructures on silicon surfaces is currently one of the most actively investigated subjects related to future molecular electronic devices.[1-7] Recently, a self-assembly approach for fabricating one-dimensional (1D) organic nanostructures on the H-terminated Si(001) surface, employing minimal intervention by the tip of a scanning tunneling microscope (STM) and a spontaneous self-directed chemical growth process, was reported by Wolkow and his coworkers.[4] This self-assembly approach has been used to fabricate various molecular lines along the dimer rows[5,6] as well as across the dimer rows[7] on the H-terminated Si(001) surface.

The self-directed growth process involves a chain reaction of alkene molecules triggered at a dangling bond (DB) site which is generated by the removal of an H atom from the H-terminated Si(001) surface.[8] To achieve the chain reaction, a radical intermediate which is initially formed by the reaction between the C-C π bond and a single DB should abstract an H atom from a neighboring Si-H surface site. Here, the stabilization of the radical intermediate determines the successful growth of 1D molecular line. Styrene,[4] vinyl ferrocene,[5] undecene,[6] and allyl mercaptan[7] exhibit the growth of 1D lines, while propylene[4] and several other alkenes[6] do not. However, it is noticeable that the energy barrier for H-atom abstraction in the former cases is still somewhat larger than the binding energy of the radical intermediate (see Figure 1), implying an easy desorption from the radical intermediate. As a matter of fact, experiments for growth of styrene,[4] vinyl ferrocene,[5] and allyl mercaptan[7] lines observed not only that some dangling bonds exhibit no growth at all, but also that longer lines can be grown at higher doses of molecules on surfaces.

In the present work, we propose a method for overcoming the existing problems in the self-directed growth process. Unlike the previous [4-7] approach which employed a single DB as the reaction site, we here employ an H-free Si dimer which can be generated with the tip of the STM. For the reaction with the H-free dimer, we chose the O-phthalaldehyde ($C_8H_6O_2$: hereafter denoted as OP) molecule containing two carbonyl groups. The radical intermediate which is formed with two Si-O bonds

between the carbonyl oxygens and the H-free Si atoms is found to be significantly more stabilized as compared to those of various [4-7] alkenes which have a single Si-C bond. As a result, the present radical intermediate successfully achieves H-atom abstraction without its desorption, thereby allowing the chain reaction. The resulting OP line which is strongly bonded to the Si dimers with two Si-O bonds per molecule will survive heating up to higher temperatures compared to the previously[4-7] reported alkene lines which have a single Si-C bond per molecule. Moreover, the structure of the OP line is characterized as single line along the dimer row, contrasting with the previous[4-6] alkene lines whose structures are not uniquely determined but mixed with single, double, and "jog" lines, depending on the direction of H-atom abstraction.

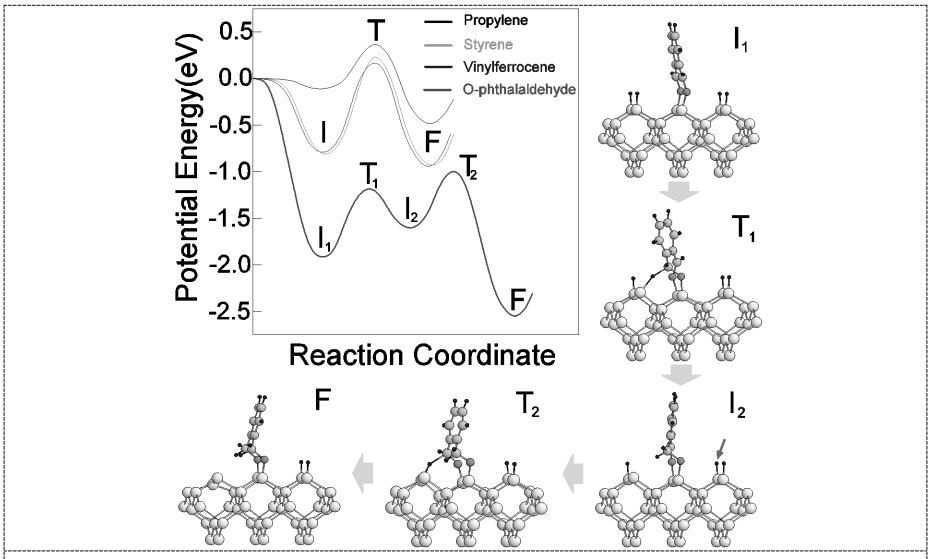

Figure 1. Calculated energy profile of H-atom abstraction for an adsorbed O-phthalaldehyde molecule on H-terminated Si(001) surface. The atomic geometries of the intermediate (I), transition (T), and final (F) states are given. The circles represent Si, C, O, and H atoms with decreasing size. For comparison, the energy profiles for propylene, styrene, and vinyl ferrocene are also given.

2. Calculational Method

We performed the total-energy and force calculations by using first-principles density-functional theory[9] within the generalized-gradient approximation (GGA). We used the exchange-correlation functional of Perdew, Burke, and Ernzerhof[10] for the GGA. The C and O (Si and H) atoms are described by ultrasoft[11] (norm-conserving[12]) pseudopotentials. The surface was modeled by the periodic slab geometry. Each slab contains six Si atomic layers and the bottom Si layer is passivated by two H atoms per Si atom. The thickness of the vacuum region between these slabs is about 14 Å. To study the reaction of an OP molecule with a single H-free Si dimer on an otherwise H-terminated Si(001) surface, we employed a 4×3 unit cell where adsorbed OP molecules are separated by two H-terminated Si dimers along the dimer row as well as by an additional H-terminated Si dimer row perpendicular to the dimer row. The electronic wave functions were expanded in a plane-wave basis set with a cutoff of 25 Ry, and the electron density was obtained from the wave functions at two k points in the surface Brillouin zone of the 4×3 unit cell. All the atoms except the bottom two Si layers were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force

components were less than 1 mRy/bohr. Our calculation scheme has been successfully applied for the adsorption and reaction of various unsaturated hydrocarbon molecules on Si(001).[13]

3. Results

We first study the reaction of an OP molecule with a single H-free dimer on an otherwise H-terminated Si(001) surface. Carbonyls in the OP molecule can initiate reaction through the oxygen lone-pair electrons. We find that the [4+2] reaction where the two C=O bonds are reacted with the π bond of the H-free Si dimer is kinetically favored over the [2+2] reaction where a single C=O bond is broken to form C-Si and O-Si bonds, similar to previous studies for the reaction of other organic molecules containing carbonyl groups on a clean Si(001) surface.[14,15] The [4+2] radical intermediate (denoted as I_1) in which the two C-O π bonds open to form two Si-O bonds and two C radicals has an adsorption energy (E_{ads}) of 1.95 eV. This value is significantly larger than the corresponding ones (0.8 and 0.77 eV, respectively: see Table 1) of the styrene[4] and vinyl ferrocene[5] cases. Such an enhanced stability of the radical intermediate of OP must greatly facilitate the growth of 1D line compared to the previous[4-7] alkene lines.

The C radicals in the I_1 state can be stabilized by H abstraction from a neighboring Si dimer. Figure 1 shows not only our calculated energy profile for the H-abstraction pathway but also the atomic geometries of the intermediate (I), transition (T), and final (F) states. There are two H-abstraction steps because of the presence of two C radicals. For the first H abstraction, we obtain E_{ads} = 1.20 eV for the transition state (T_1) which is 0.75 eV smaller than the adsorption energy at the I_1 state, yielding an energy barrier (E_b) of 0.75 eV. As shown in Figure 1, the second H abstraction at the I_2 state takes place with a relatively smaller barrier (E_b = 0.63 eV) compared to that of the first H abstraction. We note that the barrier for the reverse reaction from I_2 to I_1 is 0.41 eV, indicating that such a reverse reaction occurs more easily than the second H abstraction. However, noting that the F state is more stable than the I_1 and I_2 states by 0.59 and 0.93 eV respectively (see Table 1), the F state will be mostly occupied at temperatures above $T_c \approx 290$ K where the activation process between the I_1 and I_2 states can be feasible.[16] Here, T_c was estimated by the assumption that all the adsorption energy of the I_1 state is dissipated during the reaction, but, if some of the adsorption energy is retained, T_c is much reduced.

Table 1. Calculated adsorption energies (in eV) of the I, T, and F states (see Figure 1) for various molecules.

	I	T	F
Propylene	0.10[a]	-0.37[a]	0.51[a]
Styrene	0.78,[a] 0.8[b]	0.02,[a] -0.25[b]	0.84,[a] 0.9[b]
Vinyl ferrocene	0.77[c]	-0.18[c]	0.93[c]
O-phthalaldehyde	1.95(I_1),1.61(I_2)	1.20(T_1),0.98(T_2)	2.54

[a]Reference 17. [b]Reference 4. [c]Reference 5.

We determine the atomic structure of an infinite OP line. We find that the infinite line has E_{ads} = 2.31 eV, smaller than that (2.54 eV) of the F state. This result implies that the repulsive intermolecular interaction between adsorbed OP molecules exists possibly due to the H atoms (in the carbonyl group) pointing toward neighboring adsorbed molecules. Since the OP line is strongly bonded to the silicon dimers with two Si-O bonds per molecule, it will be stable at higher temperatures compared to the previous[4-7] alkene lines which have a single Si-C bond per molecule. Note that the calculated adsorption energy of the F state for OP is over two times greater than those for alkenes (see Table 1).

Experiments[4-6] observed that the alkene lines exhibit several kinds of structures such as single (with molecules adsorbed along one side of a dimer row), double (on both sides of a dimer row) and jog (single but with changing the adsorption side) lines depending on the direction of H abstraction. However, the present OP line is always assembled with a single line on top of a dimer row. This unique structure formation will be helpful for designing and controlling self-assembly of 1D molecular lines on the H-terminated Si(001) surface.

It is notable that in the I_2 state hydrogen may be abstracted from the opposite neighboring dimer (indicated by the arrow in Figure 1). However, we find not only that the barrier for such an H abstraction is 0.76 eV, larger than E_b = 0.63 eV for the above considered H-abstraction pathway, but also that the resulting final state (denoted as F') has E_{ads} = 1.91 eV, being less stable than the I_1 and F states by 0.04 and 0.63 eV, respectively. Thus, we can say that formation of the F state is kinetically and thermodynamically favored over that of the F' state. Note that, if the reaction of OP molecule with an isolated H-free dimer reaches the F state, the subsequent reactions take place only along one direction of a dimer row, resulting in the growth of a single OP line.

4. Summary

In summary, we have proposed a facile method for the self-directed growth of 1D molecular lines on the H-terminated Si(001) surface. This method employing a single H-free dimer instead of a single DB greatly enhances the stability of the radical intermediate, thereby facilitating the chain reaction for 1D molecular lines. We hope the proposed method to stimulate experiments for fabrication of 1D molecular lines tightly attached to the Si(001) substrate.

References

[1] Wolkow R A 1999 *Annu. Rev. Phys. Chem.* **50** 413
[2] Bent S F 2002 *Surf. Sci.* **500** 879
[3] Bocharov S, Dmitrenko O, Mendez De Leo L P and Teplyakov A V 2006 *J. Am. Chem. Soc.* **128** 9300
[4] Lopinski G P, Wayner D D M and Wolkow R A 2000 *Nature* (London) **406** 48
[5] Kruse P, Johnson E R, DiLabio G. A and Wolkow R A 2002 *Nano Lett.* **2** 807
[6] DiLabio G A, Piva P G, Kruse P and Wolkow R A 2004 *J. Am. Chem. Soc.* **126** 16048
[7] Hossain Md Z, Kato H S and Kawai M 2005 *J. Am. Chem. Soc.* **127** 15030
[8] Lyding J W, Shen T C, Hubacek J S, Tucker J R and Abeln G C 1994 *Appl. Phys. Lett.* **64** 2010
[9] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864; Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133.
[10] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[11] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
[12] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993
[13] Cho J H and Kleinman L 2005 *Phys. Rev. B* **71** 125330; Kim H J and Cho J H 2005 *Phys. Rev. B* **72** 195305; Kim H J and Cho J H 2004 *J. Chem. Phys.* **120** 8222; Cho J H and Kleinman L 2003 *Phys. Rev. B* **67** 201301(R)
[14] Hacker C A and Hamers R J 2003 *J. Phys. Chem. B* **107** 7689
[15] Hermann A, Schmidt W G and Bechstedt F 2005 *Phys Rev. B* **71** 153311
[16] Using an Arrhenius-type activation process with a pre-exponential factor of 10^{13} s^{-1}, we estimated $T_c \approx 290$ K for a feasible transition between I_1 and I_2.
[17] Kang J and Musgrave C B 2002 *J. Chem. Phys.* **116** 9907

Acknowledgments

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