

## One-dimensional molecular wire on hydrogenated Si(001)

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An important example of hybrid organic-silicon systems is the fabrication of styrene molecular wires on a H-passivated Si(001) surface. Here we theoretically demonstrate that a styrene molecule which easily adsorbs on a single H-empty site can be further stabilized (with an energy barrier of 0.88 eV) by abstracting an H atom from a neighboring Si dimer. This H-abstraction process creates another H-empty site, setting off a chain reaction that results in the growth of a styrene wire along the Si dimer row. Our simulated scanning tunneling microscope (STM) image for the resulting one-dimensional (1D) molecular wire is in good agreement with STM data. In particular, the antibonding  $\pi$  orbitals on adjacent styrene molecules overlap, thus providing “channels” that permit charge transport along this 1D wire under a voltage bias.

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The recent demonstration of ordered organic monolayer films on the Si(001) surface<sup>1–4</sup> has received widespread attention because of the possibility of various technological applications such as microscopic chemical sensors, optical devices, or biochemical monitors. This hybrid organic-silicon system can utilize the wide range of functionality of organic molecules combined with the existing Si-based infrastructure. In order to study and engineer atomic-scale structures of adsorbed organic molecules, the scanning tunneling microscope (STM) technique is very useful both for imaging and manipulating individual molecules. Moreover, first-principles calculations provide detailed information about adsorbate-surface structures and also predict the STM images of adsorbed molecules. Thus, both experimental and theoretical tools offer new opportunities for revealing the fundamental reactions involved in hybrid organic-silicon systems.

Recently, the STM study of Lopinski, Wayner, and Wolkow<sup>5</sup> observed growth of styrene molecular wires on an H-passivated Si(001) surface, determining both the orientation of the wires and the molecular spacing within these wires. For such growth of molecular wires they proposed a so-called chain reaction mechanism. Here, a styrene molecule easily reacts with a single Si dangling bond which they generated by the removal of a H atom using the tip of the STM. Subsequently, the C radical produced by the adsorption of the styrene molecule can abstract a H atom from a neighboring Si dimer, leaving another H-empty site. This H-abstraction process sets off the chain reaction to grow a one-dimensional (1D) molecular wire along the Si dimer row. The STM images showed that styrene wires formed along the Si dimer rows consist of two kinds of structures: i.e., single or double lines composing a 1D wire. Especially, in the single line, adsorbed styrene molecules clearly appear as a bright spot per molecule, where the individual spots are spaced by 3.8 Å, corresponding to the distance between dimers on the Si(001) surface. It is interesting to note that growth of styrene wires is dependent on the wire length. That is, there is some preferential growth of longer wires; some isolated Si dangling bonds exhibit no growth at all.<sup>5</sup> Despite all these experimental observations, several aspects of the spontaneous self-directed growth of styrene wires such as the

energetics for the H-abstraction process and the geometric and electronic properties of styrene wires need to be investigated for the atomic-scale fabrication of 1D molecular wires on Si(001).

We perform the total-energy and force calculations by using density-functional theory<sup>6</sup> within the generalized-gradient approximation.<sup>7</sup> The C (Si and H) atom is described by ultrasoft<sup>8</sup> (norm-conserving<sup>9</sup>) pseudopotentials. The surface is modeled by a periodic slab geometry. Each slab contains five Si atomic layers plus adsorbed styrene molecules 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 9 Å. A plane-wave basis set was used with 25 Ry cutoff, and the  $\mathbf{k}$  space integration was done with meshes of 8, 4, and 4  $\mathbf{k}$  points in the  $(2 \times 1)$ ,  $(4 \times 1)$ , and  $(2 \times 3)$  surface Brillouin zones, respectively. All the atoms except the bottom Si layer were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr. The geometry and energy of a free styrene molecule were determined using a  $12 \times 10 \times 18$  Å<sup>3</sup> supercell calculation with one  $\mathbf{k}$  point.

In this paper we present our first-principles calculation results for the formation of a styrene wire on an H-passivated Si(001) surface. The binding of an isolated styrene molecule to a surface Si atom (adsorption energy  $E_{\text{ads}} = 1.10$  eV) becomes weaker in the single ( $E_{\text{ads}} = 0.91$  eV) and double ( $E_{\text{ads}} = 0.66$  eV) lines, indicating repulsive intermolecular interactions between adsorbed molecules. According to our reaction pathway for the above mentioned H-abstraction process, the abstraction of a H atom from a neighboring Si dimer to an adsorbed styrene molecule takes place via a transition state with an energy barrier of 0.88 eV, indicating a ready thermal activation at room temperature. The optimized atomic structures of adsorbed styrene molecules in the single and double lines give buckled molecular geometries while keeping the parallel alignment of the phenyl rings. Our simulated filled-state STM images show a bright spot per molecule, originated from the tilted  $\pi$  orbitals in the topmost C—C atoms. The calculated charge density of unoccupied states reveals electronic coupling between adjacent styrene molecules, due to an extension of antibonding  $\pi$  orbitals along the 1D molecular wire.

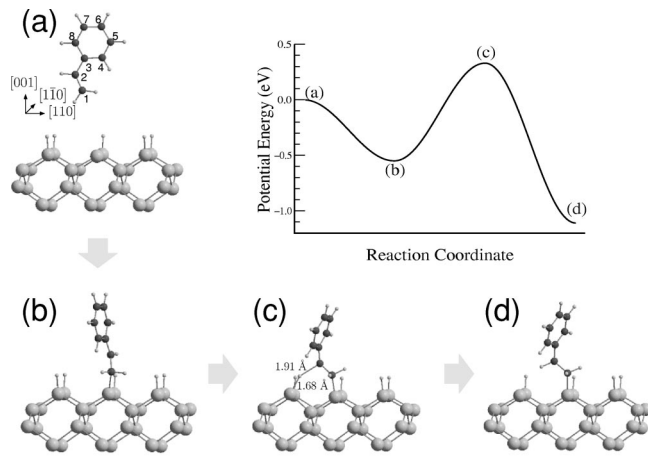


FIG. 1. Calculated energy profile of the H-abstraction process for an adsorbed styrene molecule on an H-passivated Si(001) surface. The atomic geometries at four representative points are given: (a) the initial state, (b) the intermediate state, (c) the transition state, and (d) the final state. The distances of  $d_{H_a-C_2}$  and  $d_{H_a-Si}$  are given in (c). In (c) and (d), one H atom bonding to the  $C_2$  atom is hidden behind  $C_2$ . The large, medium, and small circles represent Si, C, and H atoms, respectively.

We first study the reaction of a styrene molecule with a single Si dangling bond on an otherwise H-passivated Si(001) surface. In our calculations this reaction is simulated by employing a  $2 \times 3$  unit cell where adsorbed styrene molecules are separated by two H-passivated Si dimers [see Fig. 1(b)]. There is energetically favored hybridization between the  $\pi$  bonding state of unsaturated hydrocarbons and the single Si dangling-bond state.<sup>10</sup> Note that a free styrene molecule [Fig. 1(a)] has one  $\pi$  bond between  $C_1$  and  $C_2$  and three  $\pi$  bonds delocalized around the phenyl ring. Based on the experimental evidence,<sup>5</sup> we consider the reaction of the  $C_1=C_2$  double bond with a single Si dangling bond, where the  $\pi$  bond opens to form one Si-C bond and one C radical [see Fig. 1(b)]. We find that this intermediate state has an adsorption energy of 0.55 eV. Lopinski, Wayner, and Wolkow<sup>5</sup> proposed that the produced C radical in the intermediate state can be stabilized by H abstraction from a neighboring Si dimer. Using a 15 Si atom cluster calculation they obtained a further 0.1 eV energy release by H abstraction. To examine the energy profile for this H-abstraction process, we consider the most probable abstraction pathway by decreasing the distance between the abstracted hydrogen  $H_a$  and the  $C_2$  atom.<sup>14</sup> In Fig. 1 the calculated energy profile and the atomic geometries of the transition and final states are displayed. We obtain the energy barrier of 0.88 eV for H abstraction, whereas the reverse reaction from the final state [Fig. 1(d)] to the intermediate state [Fig. 1(b)] has an energy barrier of 1.43 eV. Experimentally, the energy barrier for the reverse reaction was estimated from styrene molecular wires as 1.15 eV. However we expect the barrier for the reverse reaction in a long chain to be less than the 1.43 eV we calculated for the isolated molecule both because the binding energy of chain molecules is less than that of an isolated molecule and because the end molecule of the chain is expected to be repelled by its neighbor toward the hydrogen.

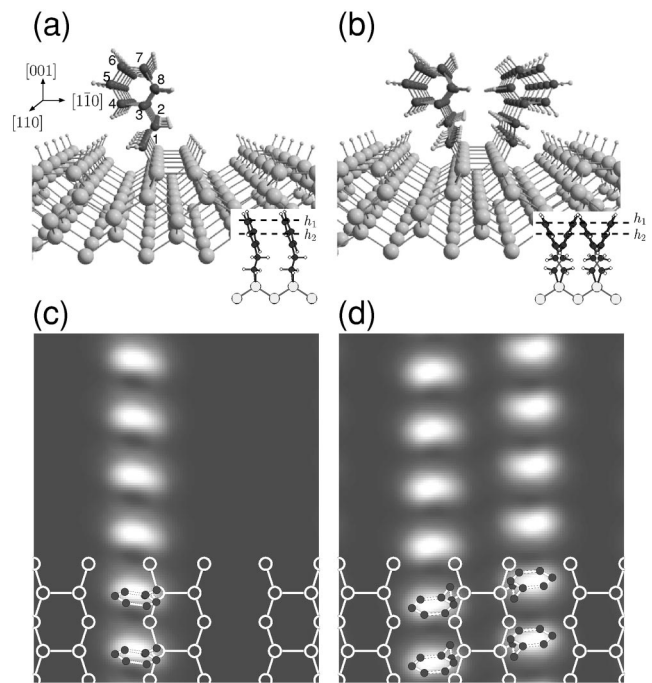


FIG. 2. Optimized structures of (a) single and (b) double lines of adsorbed styrene molecules on a H-passivated Si(001) surface. The insets in (a) and (b) show the side views from the  $[1\bar{1}0]$  direction. The simulated filled-state STM images for the structures of (a) and (b) are given in (c) and (d), respectively. The images were obtained by integrating the electron density over an energy range between  $E_{VB}$  and  $E_{VB}-2.2$  eV. The images were taken at about  $2.5 \text{ \AA}$  above the outermost C atom. The small and large circles in (c) and (d) represent the positions of the C and the first and second Si layer atoms, respectively

We note that the present adsorption energies for the intermediate state ( $E_{(b)}=0.55$  eV) and the final state ( $E_{(d)}=1.10$  eV) differ considerably from the results obtained from the cluster calculation<sup>5</sup> ( $E_{(b)}=0.8$  eV and  $E_{(d)}=0.9$  eV), although our infinite chain  $E_{(d)}$  remarkably agrees with the cluster  $E_{(d)}$  for an isolated molecule.

The energy profile in Fig. 1 implies that thermal activation at room temperature can drive H abstraction. Assuming an Arrhenius-type activation process with the usual attempt frequency of  $\sim 10^{14}$  Hz,<sup>15</sup> we estimate the reaction rate for H abstraction as  $\sim 0.175 \text{ s}^{-1}$  at room temperature, corresponding to a half-life of about 4 sec. On the other hand, the reverse reaction rate with the energy barrier of 1.43 eV is estimated as  $1.05 \times 10^{-10} \text{ s}^{-1}$ , indicating a quite slow reaction rate. Our predictions are consistent with experimental findings<sup>5</sup> that the formation of styrene wires easily occurs by a spontaneous self-directed chemical growth process and that in some styrene wires “unzipping” events by the reverse reaction were not observed even at  $300^\circ\text{C}$ .

In observed STM images,<sup>5</sup> growth of a single line along one side of a Si dimer row [see Fig. 2(a)] was frequently observed and some double lines in which styrene molecules adsorb on the both sides of a Si dimer row [see Fig. 2(b)] were also observed. We determine the atomic structure of an infinite molecular wire composed of single or double lines.

TABLE I. Calculated adsorption energy (in eV) and atomic positions (in Å) of C atoms. The values in  $(x, y, z)$  denote the displacements, relative to the Si dimer atom bonding to the  $C_1$  atom, along the  $[110]$ ,  $[1\bar{1}0]$ , and  $[001]$  directions, respectively. In the double lines the displacements of the two adsorbed styrene molecules are given together.

	Single line	Double lines
$E_{\text{ads}}$	0.91	0.66
$C_1$	(0.164, -0.884, 1.701)	(0.486, -0.816, 1.670) (-0.483, 0.817, 1.670)
$C_2$	(-0.185, -0.099, 2.974)	(-0.387, -0.918, 2.924) (0.386, 0.918, 2.927)
$C_3$	(0.127, -0.836, 4.265)	(0.311, -1.498, 4.136) (-0.317, 1.501, 4.136)
$C_4$	(-0.063, -2.225, 4.403)	(0.445, -2.894, 4.264) (-0.451, 2.897, 4.263)
$C_5$	(0.204, -2.870, 5.619)	(1.012, -3.461, 5.411) (-1.016, 3.468, 5.411)
$C_6$	(0.674, -2.140, 6.720)	(1.461, -2.639, 6.455) (-1.465, 2.645, 6.456)
$C_7$	(0.875, -0.759, 6.594)	(1.353, -1.247, 6.332) (-1.354, 1.253, 6.336)
$C_8$	(0.603, -0.118, 5.378)	(0.780, -0.683, 5.182) (-0.786, 0.689, 5.184)

Here, we employed a  $4 \times 1$  unit cell to make negligible the intermolecular interaction of adsorbed molecules perpendicular to the dimer row direction. The optimized structures of both cases are shown in Figs. 2(a) and 2(b). Each adsorption energy and atomic positions of C atoms are given in Table I. We find that the adsorption energy of the single (double) line is 0.91 (0.66) eV. Note that two styrenes adsorbed on a Si dimer are lower in energy by 0.41 eV than one adsorbed and one free styrene so that, once started, the double chain is expected to grow. We also find that upon adsorption the planar geometry of the free styrene molecule becomes buckled while bonding with the Si. The insets in Figs. 2(a) and 2(b) show that the phenyl rings are tilted from the  $[001]$  direction around the  $[1\bar{1}0]$  direction. Note that such tilting in the double lines ( $\sim 25^\circ$ ) is larger than that in the single line ( $\sim 18^\circ$ ). In the double lines the two styrene molecules bonding to the same Si dimer have the opposite directions of tilting (yielding reversed displacements in the  $[110]$  and  $[1\bar{1}0]$  directions, see Table I) in order to diminish the repulsive intermolecular interactions.

Although the growth kinetics of styrene wires is beyond the present study, we believe that styrene molecules may easily diffuse along the direction parallel to the Si dimer rows through the “valley” between the dimer rows [see Fig. 2(a)]. Similar to the step edge, growing lines might increase the diffusion barriers for crossing the lines. Thus, styrene molecules blocked by the lines will diffuse through the valley rather than across the dimer rows which may have higher corrugated barriers due to the passivating H atoms. At last, diffusing molecules in the valley find the empty H site which is located at the terminal of growing lines. In this way, we

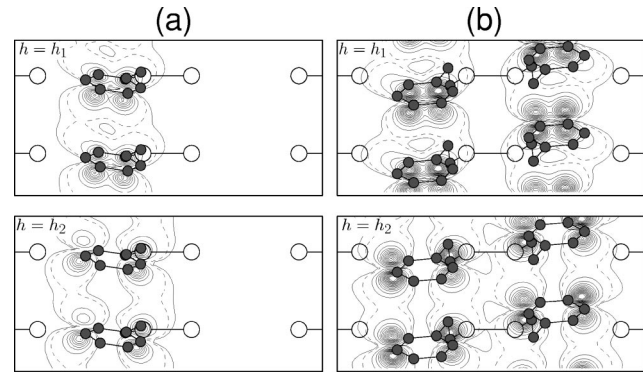


FIG. 3. Calculated charge densities of unoccupied states for (a) single and (b) double lines. Here, the charge density was integrated over an energy range between  $E_{\text{VB}}$  and  $E_{\text{VB}} + 4$  eV. For each structure the two plots at the two different heights  $h_1$  and  $h_2$  [see the insets in Figs. 2(a) and 2(b)] are displayed. The first contour line is at 1 millielectron/bohr<sup>3</sup> and the solid contour line spacing is 3 millielectron/bohr<sup>3</sup>. The dashed contour is at 1.45 millielectron/bohr<sup>3</sup>. The filled and open circles represent the positions of the C and the Si dimer atoms, respectively.

speculate that existing longer lines can grow fast because relatively more molecules blocked by longer lines diffuse through the valley, preferentially adhering to the lines. This speculative argument for growth of styrene lines can explain the STM observation<sup>5</sup> that some lines grow much longer than others.

Our simulated filled-state STM images for the infinite single and double lines are shown in Figs. 2(c) and 2(d), respectively. Here, the images mapping the electron density integrated over an energy range between the valence-band maximum ( $E_{\text{VB}}$ ) and  $E_{\text{VB}} - 2.2$  eV are taken at about 2.5 Å above the outermost C atom (2.2 eV was the voltage at which the experimental data<sup>5</sup> was taken). Both images in Figs. 2(c) and 2(d) show a single bright spot per molecule, representing the  $\pi$  orbital of the  $C_6$ — $C_7$  bond. Despite the mirror symmetry of the  $\pi$  orbital about the  $C_6$ — $C_7$  bond, the STM images show only a single bright spot on the one side, as a consequence of the tilting of the phenyl ring. We note that the bright spot lines appear nearly centered between Si dimer rows [see Figs. 2(c) and 2(d)]. All these features in the simulated STM image of the single line are in good agreement with STM data, whereas the feature of a double-row zigzag chain in the double lines [Fig. 2(d)] was not clearly resolved in STM data.<sup>5</sup>

It is expected that the parallel alignment of the phenyl rings in the single [Fig. 2(a)] and double [Fig. 2(b)] lines may have overlap between  $\pi$  orbitals. Using extended Hückel calculations Lopinski, Wayner, and Wolkow<sup>5</sup> found that the lowest unoccupied molecular orbitals in the single line (simulated by a finite cluster modeling) have considerable electronic coupling between adjacent molecules. In order to examine such possibility in long molecular lines, we calculate the charge density of unoccupied states integrated over an energy range between  $E_{\text{VB}}$  and  $E_{\text{VB}} + 4$  eV. The results for the single and double lines are shown in Figs. 3(a) and 3(b), respectively. Our calculated charge densities at the



two different heights  $h_1$  and  $h_2$  [see the insets in Figs. 2(a) and 2(b)] show electronic coupling between adjacent styrene molecules. We see that a path exists along the chain over which the density stays above 1.45 millielectrons/bohr<sup>3</sup>. For comparison, the average conduction electron density in potassium is 2.08 millielectrons/bohr<sup>3</sup> so we conclude that if electrons can be injected into the styrene wires and if there is a barrier to their dropping to the bottom of the Si conduction band, the wire could conduct. However, this result cannot be compared with numerical results from the cluster calculation which were not given in Ref. 5.

In summary, on the basis of density-functional theory calculations we have demonstrated that growth of styrene molecular wires spontaneously takes place with thermal activation, confirming the recently proposed chain reaction

mechanism.<sup>5</sup> The present theory provides detailed information about the geometric and electronic properties of a styrene wire. Especially, the electronic properties of this 1D molecular wire, which show the extent of antibonding  $\pi$ -orbital overlap between adjacent molecules, suggest that attempts to measure their conductivity, with a view toward using them as 1D molecular nanoconductors, might be fruitful.

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<sup>10</sup>Although a small barrier could exist between the initial state [Fig. 1(a)] and the intermediate state [Fig. 1(b)], the adsorption of styrene on Si(001) differs from that of acetylene (Ref. 11), cyclopentene (Ref. 12), and 1,3-cyclohexadiene (Ref. 13) on a clean Si surface. In those cases a somewhat complicated path is required to break the Si dimer  $\pi$  bond and bind two carbons to the dimer, resulting in an energy barrier. In the present case a single carbon bonds with a Si dangling bond.

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<sup>14</sup>The reaction path was determined by constraining the H<sub>a</sub>—C<sub>2</sub> separation to a series of values while relaxing all the forces to less than 1 mRy/bohr.

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