How to Fabricate a Surface-Grafted Polythiophene on H-Si(100) 2×1 Surface via Self-Assembling and in Situ Surface Polymerization: A Theoretical Guide

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ABSTRACT: Based on density functional theory calculations, we have studied the self-assembled growth of thiophene substituted alkenes, [H$_2$C–CH–(CH$_2$)$_n$–thiophene] on hydrogen-terminated H-Si(100) 2×1 and H-Ge(100) 2×1 surfaces into aligned one-dimensional (1D) molecular arrays which are chemically bonded to the surfaces via the alkane chain. The thiophene rings at the top end of the molecular arrays are situated side by side and can undergo an in situ polymerization reaction into polythiophene once radicals are introduced to the thiophene rings, thereby forming polyalkylthiophene-Si/Ge(100) 2×1 surface-grafted polymers. Like most of conductive polymers, these surface single polymer chains exhibit semiconducting character and can be made conductive either by p-doping or by applying an external electric field. More importantly, both surface-grafted polymers and substrates retain their electrical properties, and the polythiophene chains are the sole conductive channels in the structures. Our findings put forth a new way to fabricate conductive polymeric molecular wires on traditional semiconductor substrates, and could find potential application in nanoelectronic devices.

1. INTRODUCTION

In the past decades, scientists and engineers have been struggling to fabricate single conductive molecular wires or conductive polymer chains on traditional semiconductor substrates in order to satisfy the ongoing miniaturization of electronic devices. Recently, using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM),1–2 experiments have demonstrated that many olefins are able to self-assemble on a hydrogen-passivated H-Si(100) 2×1 surface to form one-dimensional (1D) aligned molecular arrays. For example, Lopinski et al. have proven in their experiments that styrene can grow into 1D molecular array on a H-Si(100) 2×1 surface.3 Via ethenyl group, a styrene molecule bonds easily with a H-empty silicon site, created by atomic force microscopy (AFM) or scanning tunneling microscopy (STM) nanopatterning technologies. The adsortion breaks the ethylene C=C π-bond and generates a C-centered radical that can extract a H atom on the adjacent surface Si atom to form ethane, resulting in a new H-empty silicon site for subsequent styrene adsorption. As such radical chain reaction process,4–7 a 1D surface absorbed phenyl ethane molecular array is formed eventually. Other examples like allyl mercaptan,8 long chain alkene (C$_8$=C$_4$),9 benzaldehyde,10 and phenylacetylene (PA)11 have been demonstrated to self-assemble and form 1D molecular arrays on H-Si(100) 2×1 surfaces.

Following the same mechanism, a thiophene-substituted alkene, H$_2$C–CH–(CH$_2$)$_n$–thiophene [Figure 1a], should be able to adsorb to a H-empty silicon site on either H-Si(100) 2×1 or H-Ge(100) 2×1 surfaces and further grow into a 1D thiophene-substituted alkane molecular array along the dimer row [011] direction (Figure 1). Based on density function theory (DFT) calculations, in this study we investigated the adsorption reaction paths for H$_2$C–CH–(CH$_2$)$_n$–thiophene, including ethylene (n = 0), propylene (n = 1), butylene (n = 2), and amylene (n = 3) on H-Si/(100) 2×1 and H-Ge/(100) 2×1 surfaces. We demonstrate that it is very feasible for these H$_2$C–CH–(CH$_2$)$_n$–thiophene molecules to adsorb and grow into 1D aligned molecular arrays along [011] direction because the molecular adsorption energies are much higher than activation energies for molecular array growth.

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These molecular arrays are chemically bonded to the surfaces via the alkane chains; meanwhile, the thiophene rings are located side by side at the top end of the molecular array and can then polymerize into polythiophenes if radicals are introduced by AFM or STM tips, eventually forming polyalkylthiophene-Si/Ge(100)2\times1 surface-grafted single-line polymers. The newly formed surface-grafted polythiophene chains are partially conjugated and exhibit intrinsic semi-conducting characters as with most conductive polymers. They can be made to be conductive either by p-doping or by applying an external electric field (EEF). The band gaps and the electrical conductivities will depend on the dihedral angles of adjacent thiophene rings among polyalkylthiophene-Si/Ge(100)2\times1, which are subjected to the length of alkanes linked to the surfaces. It is also found that partially conjugated polythiophene chains are the sole conductive channels in the polymer/surface structures.

Single conjugated polymers, especially polythiophene and its derivatives, such as poly(3-alkylthiophene)s, have been considered as promising molecular wires for next generation nanoelectronics, solar cells, light emitting diodes, and sensors.\(^\text{12-22}\) Great efforts have been invested in single polythiophene chain fabrications on surface substrates. For example, Sakaguchi et al. have shown experimentally that two different kinds of thiophene monomers on an iodine-covered gold surface can create highly ordered conjugated copolymer chains with different electronic structures by electrochemical polymerization.\(^\text{23,24}\) While, the synthesized polymer chains adhere to the Au surfaces with van der Waals interactions only and thus can be peeled off when the temperature is increased. Therefore, it is not meaningful for real application. As Lipton-Duffin et al. indicated that one of the greatest challenges in surface chemistry is to assemble aromatic building blocks into ordered structures that are mechanically robust and electronically interlinked, i.e., held together by covalent bonds.\(^\text{25}\) They have demonstrated the synthesis of polyphenylene molecular wires by surface-confined polymerization on crystal Cu surfaces.\(^\text{26}\) However, fabrication of a conductive polymer chain on a metallic surface is not very useful for electronic applications.

In comparison, surface-grafted single-line polyalkylthiophene-Si/Ge(100)2\times1 are chemically bonded to the Si or Ge surfaces via the alkane chains and they are mechanically robust and electronically interlinked. Interestingly, both surface polymers and substrates retain their electrical properties based on their calculated band structures, suggesting there is little electron transfer between the surface polymers and substrates. The surface-grafted polymers and underlying substrates seem to be “independent of each other”, which is an ideal model of a conductive molecular wire on a traditional semiconductor substrate.

There have been several theoretical studies on the self-assembling mechanism of alkenes on silicon surfaces to form molecular arrays, where aligned molecules are absorbed on Si surfaces but they are not interlinked.\(^\text{27,28}\) Only very recently, we proposed a surface in situ polymerization reaction for self-assembled 4-hydrazinyl-3-(pyridin-4-ylmethyl)-benzaldehyde (HPyMB) molecules to produce a conductive molecular wire based on pyridines alternating adsorption on a line of exposed surface Si atoms.\(^\text{29}\) In this work, we extended the study to thiophene-substituted alkanes self-assembling on H-Si/Ge surfaces, based on the experimental approved olefins surface self-assembling mechanism, to produce single molecular wires (surface-grafted polymers) via in situ polymerization reaction subsequently. Our work provides a new perspective on the fabrication of conductive molecular wires or polymer chains on
traditional semiconductor substrates and uncovers the mechanism of the molecular wire conductivity.

2. COMPUTATIONAL MODELS AND METHODS

We used a 2 × 2 orthogonal supercell model for both H-Si(100)-2×1 and H-Ge(100)-2×1 surfaces with five silicon/germanium layers. The atoms in the three bottom layers are fixed and the bottom layer is passivated with hydrogen to mimic the bulk Si/Ge. On the top surface, the Si/Ge atoms are saturated with hydrogen atoms with one H-empty site. The vacuum space is more than 10 Å. The model for H2C═CH-(CH2)n-thiophene absorbed on the H-Si(001)2×1 surface with a C-radical is depicted in Figure 1b.

All calculations were performed within the framework of a spin-polarized plane-wave DFT implemented in the Vienna ab initio simulation package (VASP). We adopted Perdew-Burke-Ernzerhof functional for exchange-correlation, and projector augmented wave potentials were used to describe the electron–ion interactions. The electronic wave functions were expanded in plane-wave basis with a cutoff energy of 400 eV. The Brillouin-zone was sampled 5 × 3 × 1 for geometry optimization and a 11 × 5 × 1 grid for band structure calculations of the polyalkylthiophene-Si/Ge(001)2×1 structure. Convergence was reached when the Hellmann–Feynman forces on each atom are less than 0.02 eV/Å.

We used the climbing-image nudged elastic band (cNEB) method to locate the transition states (TS) for the H-extraction reactions of the adsorbed molecules to grow into molecular arrays. The calculations were performed within a 2 × 2 supercell and a k-mesh of 5 × 3 × 1 as mentioned above. Besides, vibrational calculations were performed to confirm the transition states in the molecular growth using cluster models, where fixed SiH3/GeH3 group was used to mimic the superlattice surfaces in supercells of 17 × 17 × 20 Å3 (for n = 0–2) and 17 × 17 × 25 Å3 (for n = 3), respectively (see Figure S1 in the Supporting Information). The effect of an external electric field (EEF) was simulated via an artificial dipole sheet placed in the middle of the vacuum normal to the Si/Ge(001) surfaces (Figure 1f).

3. RESULTS AND DISCUSSION

In experiments, using AFM/STM nanopatterning/lithography technologies, a selected surface hydrogen atom can be kicked off from a H-Si(001)2×1 or a H-Ge(001)2×1 surfaces [H-Si/Ge(001)2×1], to create an empty site with a Si/Ge dangling bond (DB). A thiophene substituted ethylene, H2C═CH-thiophene (as an example, n = 0), can bond to the H-empty site without any energy barrier and thereafter generate a C-centered radical intermediate [Figure 1b]. The adsorption is exothermic, and the calculated adsorption energies are 0.62 and 1.06 eV for intermediate state and the final state, respectively, after H-abstraction according to the following formula, E_{ads} = E[atom] + E[sheet] − E[molecule/surface]; here $E[\cdot]$ represents the energy of an isolated molecule [H2C═CH-(CH2)n-thiophene], a H-Si/Ge(001)2×1 surface with a H-empty site, and the total energy of a H-Si/Ge(001)2×1 surface with an absorbed molecule, respectively. E_{ads} gives the average adsorption energy of the first absorbed molecule, which is comparable to those Si surface absorption energies reported for alkenes such as styrene.

Different from the sulfur atoms in mercaptans, the sulfur atoms in thiophene are inert and they are not able to bond to the H-empty sites. To clarify it, we calculated the S–Si bonding energy of a 3-allylthiophene to a surface silicon atom at a H-empty site via its thiophene sulfur atom and got the adsorption energy of 0.05 eV. In comparison, the bonding energy of an ethenyl bonding to a surface Si atom (C–Si) is about 1.0 eV. Therefore, it is not possible for thiophene sulfur instead of ethenyl group to bond to surface silicon.

Actually, we have considered all possible reactions which may occur on the surface or between the absorbed molecules, such as the second C atom of ethenyl (C═C) to absorb on surface silicon atoms, leaving the end methylene (H2C) group as a radical. The absorption energy of second C atom to bond with the surface Si atom is about 0.1 eV which is much weaker than the first C atom with surface (see Table 1). More importantly, comparing to the first C atom, the steric obstruction is dramatically increasing for the second C atom to bond to the surface Si atom and it is kinetically unfavorable. Therefore, such absorption has not observed in experiments. The end carbon of double bond in 3-allylthiophene is the sole reactive point for H-Si/Ge(001)2×1 surfaces. It is also hardly for C-centered radical to abstract hydrogen across the row because the distance between the carbon radical and surface H atom cross row is about 5.3 Å. In addition, the distance between the C-centered radical and the second C of neighboring absorbed H2C═CH-(CH2)n-thiophene is about 3.9 Å which is too far away, and the polymerization reaction cannot occur between them. Because a radical is very reactive, there should be some side reactions.

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Table 1. Adsorption Energy for Intermediate State ($E_{ads}$−1) and for the State after H-Abstraction ($E_{ads}$−2), Molecular Growth Activation Energy for H Extraction ($E_m$), Energy Differences between Homolateral and Heterolateral Molecular Arrays (ΔE), and the Polymerization Energy for Heterolateral ($E_{hetero}$) and Homolateral ($E_{homo}$) Structures of Thiophene Substituted Alkenes on Si(100)-2×1 and Ge(100)-2×1 Surfaces

<table>
<thead>
<tr>
<th>n</th>
<th>Si(100)-2×1</th>
<th>Ge(100)-2×1</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$E_{ads}$−1 (eV)</td>
<td>0.62</td>
<td>0.28</td>
</tr>
<tr>
<td>$E_{ads}$−2 (eV)</td>
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<td>1.19</td>
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<tr>
<td>$E_m$ (eV)</td>
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<tr>
<td>ΔE (eV)</td>
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<td>$E_{ads}$ (eV)</td>
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<td>0.77</td>
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<tr>
<td>$E_{ads}$ (eV)</td>
<td>1.76</td>
<td>1.76</td>
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</table>

ΔSchematic surface reactions can be found in Figure 2.
which can terminate the 1D growth reaction. This is another topic, and we may consider that in our future work.

To study the growth of the molecular array, we calculated the activation energy for a C-centered radical intermediate [Figure 1b] to extract one H atom from the adjacent surface silicon atom in the neighboring Si dimer. The energy profile of a thiophene substituted ethylene \((n = 0)\) growth reaction on a H−Si(001)2×1 surface is depicted in Figure 2. The initial adsorption of a H₂C≡CH-thiophene on a H-empty site, where a Si dangling bond is present, is spontaneous with the initial adsorption energy of 0.62 eV, which results in the formation of a C−Si bond after the breaking of the ethylene C=C \(\pi\)-bond. Subsequently, a C-centered radical is formed, that is a very reactive intermediate state (IS) and will abstract one H atom from the adjacent Si atom to saturate itself forming ethane. The calculated energy barrier for this process is 0.57 eV, which is lower than the initial adsorption energy and much lower than the adsorption energy (1.06 eV, after H abstraction from the neighboring Si site). We therefore can expect that the initial state is able to trespass the transition state (TS) to reach the final state (FS) quite easily and simultaneously create a new H-empty site for the next molecular absorption. As this process continues, a thiophene substituted ethane molecular array is formed on the silicon surface eventually. The absorption and activation energies for the reaction of H₂C≡CH-(CH₂)ₙ-thiophene on H-Si(001)2×1 are comparable to olefins grown on silicon surface reported previously. For example, styrene has been proven to be able to absorb and self-grow into 1D molecular array on H-Si(001)2×1 following the same scenario.

We are also noted that H abstraction may occur from the same Si dimer; therefore we calculated the energy barrier of H abstraction from the same Si dimer for \(n = 0\). The calculated energy barrier is 0.80 eV, which is much higher than 0.57 eV for H abstraction from the neighboring Si dimer, indicating that the radical chain reaction along the [011] direction is more favorable and predominant. Furthermore, high energy barrier of 0.80 eV implies the H abstraction from the same Si dimer could occur at higher temperatures, which is in accordance with an experimentally observed double-line molecular array for styrene. We may consider such two-direction growth in our future work.

We next studied the effect of alkene chain length on molecular array growth. It is found that the chain length only shows a weak effect on the activation energies \(E_{\text{act}}\) in which longer chains show only a slightly lower \(E_{\text{act}}\). In addition, based
on the cluster models mentioned above, we performed transition states (TS) vibrational mode calculations for all eight reactions (four on silicon and four on germanium surfaces). The results show only one soft mode with imaginary frequency for each of the transition state in H-extraction reaction. Each eigenvector of the soft mode corresponds to the motion of H atom on Si/Ge surfaces toward the C-centered radical (Figure S2 in SI), confirming that the TSs are identified correctly.

Actually, when the molecules grow on surfaces, the newly formed molecular arrays can bend to different directions, thereafter forming different configurations. Here, we are focusing on two specific configurations, namely homolateral and heterolateral structures with respect to the [011] direction on the Si surface [Figure 1cd]. The homolateral structure refers to the one that all alkanes absorb on the surface in parallel, while the heterolateral structure is the one that the adjacent absorbed alkanes bend to opposite directions. As expected, the heterolateral structures are more stable, and the energy difference between the homolateral and heterolateral structures becomes larger with the increase in the alkane chain length (n). This is because the increased degree of freedom in longer alkane chains reduces the intramolecular and intermolecular repulsion (Table 1). To study the intermolecular interactions, we calculated the average adsorption energies after first, second, and third HCH-(CH2)n-thiophene adsorptions and molecular array formations for heterolateral configuration when n = 0–3 on silicon surface using 4 × 2 supercell, and the results are given in Table S1 in the Supporting Information. The values of the average adsorption energies after first, second, third are very close, meaning that the intermolecular interactions absorbed molecules are not prominent. The average adsorption energies of molecular arrays are slightly lower than that after third isolated molecule.

It is noted that in both heterolateral and homolateral structures, the thiophene rings are situated side by side at the top end of the molecular array. Considering longer alkane chains may have more possible conformations, we did not consider the cases for n > 3. Using nanopatterning technologies in surface science, radicals can be created on a surface adsorbed molecule using AFM or STM tips or even UV light. Once a radical is introduced onto one of the thiophene rings, an in situ polymerization reaction occurs spontaneously, forming polyalkylthiophene/Si/Ge(100)2×1, a surface grafted single-line polymer structure, as in most radical polymerization reactions. Nowadays, there have been a few examples on surface grafting control reactions using AFM tips or UV light activations. Goda et al. reported a biomimetic phosphorycholine polymer grafting from polydimethylsiloxane surface using photoinduced polymerization. Lisboa et al. deposited polypyrrole (PPy) films done by grafting allylamine or acrylic acid using UV light radical activation. Radical-introducing essentially increases the internal energy of the molecules and allows them to overcome the energy barriers for polymerization. However, due to the space constraints, the newly formed polythiophene cannot be perfectly coplanar [Figures 1ef and 3]. The polymerization is an endothermic process, and the relevant heats/energies needed are listed in Table 1. It is seen that the energies required for the heterolateral structure are much lower than that for homolateral, and decrease along with increasing n, the chain length of alkanes. This is because longer chains relieve the tensions in the polymer structures and, hence, enable polythiophene to be more coplanar. Figure 3 shows the dihedral angles between two adjacent thiophene rings in different polyalkylthiophenes on silicon surfaces. Indeed, the more coplanar the thiophene rings, the lower the energy required. It must be noted that all these polymerization energies are lower than the adsorption energy, and for polypentylthiophene (n = 3), Ehet

### Table 2. Band Gaps (Δ) for Polyalkylthiophenes on H-Si(100)2×1 and H-Ge(100)2×1 Surfaces, Respectively, and Δ Values under a 0.2 V/Å External Electric Field (EEF) Normal to the Surfaces

<table>
<thead>
<tr>
<th>n</th>
<th>Δ (eV) Si(100)-2×1</th>
<th>Δ (eV) Ge(100)-2×1</th>
<th>Δ (eV) at EEF = 0.2 V/Å Si(100)-2×1</th>
<th>Δ (eV) at EEF = 0.2 V/Å Ge(100)-2×1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.28</td>
<td>0.97</td>
<td>0.87</td>
<td>0.86</td>
</tr>
<tr>
<td>1</td>
<td>1.27</td>
<td>0.89</td>
<td>0.87</td>
<td>0.67</td>
</tr>
<tr>
<td>2</td>
<td>1.12</td>
<td>0.53</td>
<td>0.86</td>
<td>0.65</td>
</tr>
<tr>
<td>3</td>
<td>0.92</td>
<td>0.27</td>
<td>0.86</td>
<td>0.39</td>
</tr>
</tbody>
</table>

structure of the pristine H-Si(100)2×1, we found the surface polymers did not obviously affect the substrate band structures by only shifting the Fermi level [Figure 4a–d]. This observation indicates little electron transfer between polyalkylthiophene chains and the substrates. Although the surface-grafted polymers are chemical bonded to the surfaces, both...
polymers and substrates seem to retain their original electron structures and exhibit independent electronic properties, which actually are ideal for molecular wires on semiconductor substrates.

This unique feature is further confirmed by comparing the band structures of (1) a single perfect polythiophene chain (the dihedral angles between adjacent thiophene rings, $\theta = 180^\circ$), (2) a perfect H-Si(100)2×1 surface, (3) polypentylthiophene/Si(001)2×1 structure, and (4) the polypentylthiophene chain after removing the silicon substrate (Figure 5). Interestingly, the band structure (3) resembles the combination of (2) and (4), indicating the intrinsic electronic structures of surface polymers and the substrates changed little. At the same time, the band structures of (1) and (4) look very similar; implying the properties of the surface polypentylthiophene chain should be close to that of the perfect coplanar polythiophene.

Figure 4. (a–d) Band structures of the polyalkylthiophenes/Si(100)2×1 and (e–h) band structures under EEF at 0.2 V/Å. Red and black circles represent the components of polyalkylthiophenes and silicon substrate, respectively. The size of the circles denotes the contributions from different components.

Figure 5. (a) Optimized structure of pure polythiophene chain and (e) its band structure; (b) H-Si(001)2×1 structure and (f) its band structure; (c) a polypentylthiophene/Si(001)2×1 surface-grafted polymer and (g) its band structure; (d) a pure organic polypentylthiophene chain and (h) its band structure. Red and black dots are the components of organic molecules and inorganic substrate, respectively.
Similar to other conductive polymers, these surface-grafted single-line polyalkylthiophenes are semiconductors in the natural state according to their band structures given in Figures 4 and 5. In real application, the polymers must be linked between two electrodes with applied electrical voltages, where electrons/holes are injected into the conductive polymers. It must be pointed out that polyalkylthiophenes/Si(001)2×1 structures are the real conductive molecular wire on the silicon surfaces only when the polythiophene chains are confirmed as the sole conductive channels. Moreover, the activation energies are much lower than the adsorption energy required for growing 1D molecular arrays because the growing energy is low on the silicon surfaces based on DFT calculations. According to the reaction mechanism, the in situ polymerization on H-Si(100) and H-Ge(100) provides a theoretical guide to fabricate ideal molecular wires on traditional semiconducting surfaces, which could find potential applications in molecular electronic devices.

4. CONCLUSIONS

In this work, we have studied self-assembled growth of a series of homologue, H2C=CH-(CH2)n-thiophene (n = 0–3) and the in situ polymerization on H-Si(100) and H-Ge(100) surfaces based on DFT calculations. According to the reaction energy profiles, we proved that H2C=CH-(CH2)n-thiophene can grow into 1D molecular chains because the growing activation energies are much lower than the adsorption energies, especially on the silicon surfaces. Furthermore, irreversible in situ polymerization reactions can occur within the thiophene rings located at the end top of the molecular arrays once radicals are introduced into the thiophene rings, forming polyalkylthiophenes/Si(001)2×1. These single polymeric chains are covalently bonded to the surfaces via strong covalent bonds and could be classified as a surface-grafted polymer. Interestingly, both polymers and substrates retain their own major electronic characteristics. In addition, these surface polymers can be made semiconductive by hole doping or applying an external electric field. More importantly, the polythiophene chain is the sole conductive channel in the system. Our finding provides a theoretical guide to fabricate ideal molecular wires on traditional semiconducting surfaces.

5. ACKNOWLEDGMENTS

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5. REFERENCES


5. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b08389.

Cluster model used for transition state location (Figure S1), the soft mode corresponding to the transition state (Figure S2), and the adsorption energies for molecular arrays (Table S1). (PDF)

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Notes

The authors declare no competing financial interest.


