

Dry Thienylation of the Silicon (111)–(7 × 7) Surface

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Received September 20, 1999

The binding of functional organic molecules onto solid substrates plays significant roles in developing advanced optics, microelectronics and sensors.¹ It is possible to design and create organic/solid interfaces with chemical and biological functionalities by surface modifications.² One modifier that offers promise for the improvement of the electron and energy transfer through the organic/inorganic interfaces is thiophene.³ Conjugated polythiophene and oligothiophene have recently been used as active layers by thin film deposition in electronic devices, such as field-effect transistors (FETs)⁴ and light-emitting diodes (LEDs).⁵ Alternatively, the active layers with extended conjugation on a semiconductor surface can be achieved by surface thienylation involving a robust covalent interaction between thiophenes and the surface atoms of a semiconductor. To our knowledge, only the thienylation of a silicon surface by a wet-chemistry method has been reported,⁶ where the covalent attachment of thienyls was achieved by a very slow reaction of thienyllithium with the prehalogenated silicon surfaces.

We report a facile method for the direct and dry thienylation of the silicon(111) surface under ultrahigh vacuum (UHV) conditions. Our results show that the covalent binding of thiophene molecules onto the silicon surface can be achieved by vapor adsorption. The annealed silicon (111) surface is (7 × 7)-reconstructed, which presents a rich array of electronically inequivalent reaction sites,⁷ providing opportunities to explore the nature of local environments on the surface chemical reactions.⁸ On the basis of combined STM and HREELS studies, we show direct evidences for the [4 + 2] cycloaddition of thiophene molecules to the adjacent adatom–rest atom pairs on a Si(111)–(7 × 7) surface. The elucidation of the molecular mechanisms involved in this approach can provide profound understanding of the important issues regarding the construction of molecular devices or extending conducting wires from Si surfaces.

Previous experimental and theoretical works have shown the feasibility of a [4 + 2] cycloaddition of butadienes on the dimer-ordered Si(100)–(2 × 1) surface, where the “Si=Si” dimers can undergo cycloaddition reactions with butadienes in analogy of

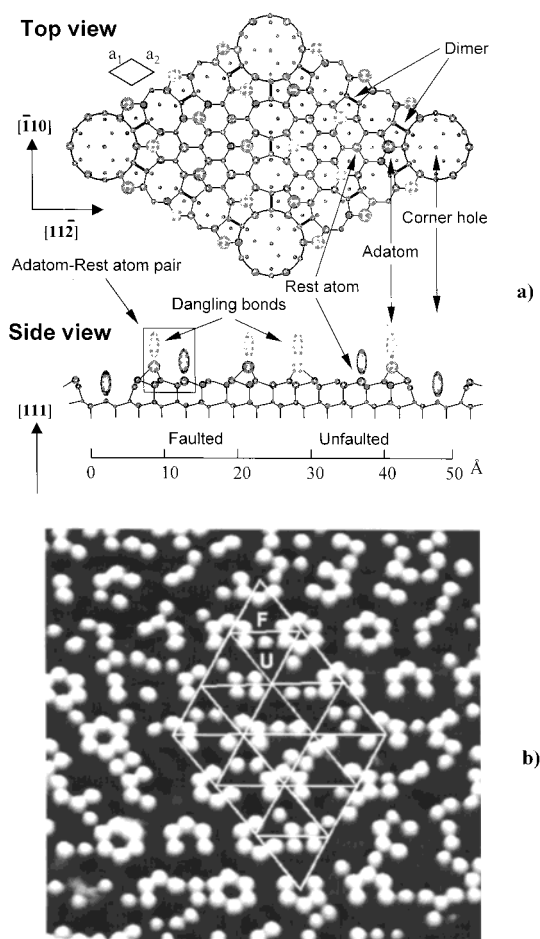


Figure 1. (a) Dimer-adatom-stacking-fault (DAS) model of a Si(111)–(7 × 7) unit cell proposed by Takayanagi et al. (ref 7). Only adatoms, rest atoms, and corner hole atoms have dangling bonds. (b) STM image (~160 Å × 160 Å, $V_S = 1.7$ V, $I_T = 0.15$ nA) of a Si(111)–(7 × 7) surface after a 5.0 L thiophene exposure. The darkened regions are due to the chemisorbed thiophene quenching the dangling bonds on surfaces.

“C=C”.⁹ In a recent study of 1,3-dienes adsorption on Si(100) using STM and FTIR,¹⁰ a surface diradical mechanism was proposed to describe the adsorption reaction between 1,3-dienes and the silicon dimer on the surface. In our case, we studied the Si(111)–(7 × 7) surface. It has been both experimentally and theoretically shown that the electron occupancies for the spatially isolated rest atoms and adatoms on Si(111)–(7 × 7) are 1.5–2 and about 0.5 electrons,¹¹ respectively. The unique geometric and electronic features of the adjacent rest atom–adatom pair (see Figure 1a) imply a “diradical site” for surface reaction.¹² On the other hand, thiophene is documented as one of the least reactive dienes in solution cycloaddition reaction due to its high aromaticity.¹³ Nevertheless, a few experimental and theoretical studies have suggested that the cycloaddition of thiophene as a diene can be facilitated by the use of highly reactive electron-deficient dienophiles, or undertaking reactions at a high pressure.¹⁴ Thiophene has a high π -electron density. In addition, the electron

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density of the highest occupied molecular orbital (HOMO) is mostly concentrated at its α -positions. These electronic characteristics make it highly susceptible to electrophilic attack at the 2,5-positions.¹⁵ Thus, the electron-deficient dangling bonds of the rest atom-adatom pair are expected to interact with the electron-rich 2,5-positions of thiophene when thiophene molecules approach the Si(111)-(7 × 7) surface.

The clean Si(111)-(7 × 7) surfaces were prepared by cycles of Ar-ion bombardment (500 eV, 30 min, 20 $\mu\text{A}\cdot\text{cm}^{-2}$) and final annealing at 1200 K for 10 min in the ultrahigh vacuum (UHV) systems. The direct thienylation was achieved by exposing gaseous thiophene molecules through a precision leak valve onto the sample surfaces, which were subsequently subjected to STM and HREELS investigations. The purity of thiophene was verified in situ using an UTI-100 mass spectrometer.

The STM images for the thiophene exposed Si(111)-(7 × 7) show darkened features, indicating the saturation of the dangling bonds and the elimination of electron density at these sites. Upon initial thiophene adsorption, preferential adsorption on the center adatom sites on faulted halves is observed. This can be understood by considering the higher electrophilicity of the adatom sites on faulted halves and a smaller steric strain induced by thiophene binding at center adatom sites.¹⁶ At saturation exposure (5.0 langmuir, 1 langmuir = 1 × 10⁻⁶ Torr·s, see Figure 1b), substantial adsorption also occurs on unfaulked halves. However, the preference of center adatoms over the corner adatom sites is still obvious. By counting up the darkened sites for adsorbed thiophene, the saturation coverage is estimated to be ~0.12 ML. On the average, this corresponds to three thiophene molecules per half unit-cell. The equal number of adsorbed thiophene molecules and the rest atoms present on the surface strongly suggests a bridged-geometry for adsorbed thiophene.¹⁷

The vibrational HREEL spectra for both multilayer and monolayer thiophene on Si(111)-(7 × 7) taken at 110 K are shown in Figure 2. The multilayer thiophene was prepared by condensing excessive (3.0 Langmuir) thiophene onto Si(111)-(7 × 7) at 110 K, which was warmed to 300 K to give the chemisorbed monolayer thiophene.¹⁸ In the temperature range studied, no energy losses around 2055 cm⁻¹ (Si-H) were observed, suggesting the nondissociative nature of thiophene adsorption. For comparison, the isotopic HREEL spectra for 2,5-deuterated-thiophene are also shown.

The spectral features characteristic of the physisorbed multilayer thiophene on Si(111)-(7 × 7) were observed in Figure 2c. The single vibrational loss at 3088 cm⁻¹ is assigned to the aromatic C(sp²)-H stretching vibration in thiophene. After warming the above sample to 300 K to desorb physisorbed thiophene, dramatic spectral changes appear in Figure 2a. Two resolved loss features at 2916 and 3048 cm⁻¹ can be clearly observed, corresponding to C(sp³)-H and C(sp²)-H stretching vibrations, respectively.²⁰ The splitting of the single vibrational loss at 3088 cm⁻¹ into resolved double loss features at 2916 and 3048 cm⁻¹ indicates a rehybridization of chemisorbed thiophene molecules. The vibrational spectrum for the multilayer 2,5-deuterated thiophene (Figure 2d) shows an additional vibrational

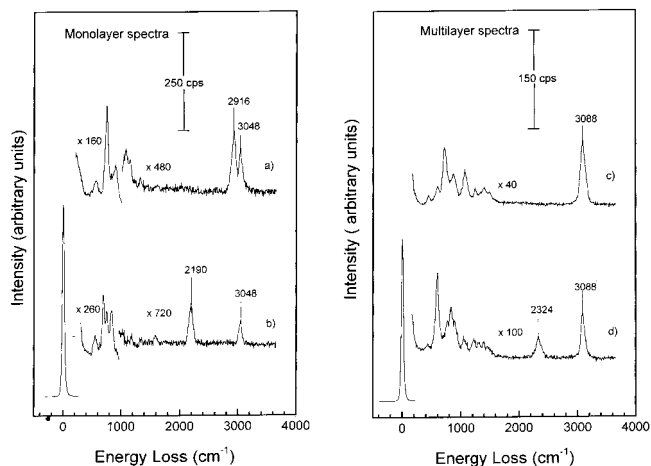


Figure 2. HREEL spectra for monolayer and multilayer thiophene on Si(111)-(7 × 7). (a) monolayer thiophene, (b) monolayer 2,5-d₂-thiophene, (c) multilayer thiophene (3.0 L), and (d) multilayer 2,5-d₂-thiophene (3.0 L). The primary electron beam with an energy of 5 eV impinges on the surface at 60° from the surface normal. The scattered electrons were detected at the specular direction. The resolution of the spectrometer (fwhm of the elastic peak) is ~5–6 mV.

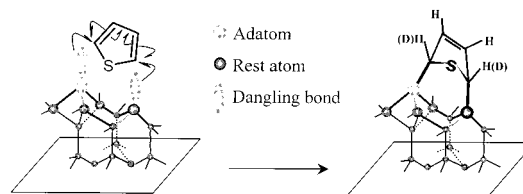


Figure 3. Schematic diagram for the dry thienylation of the Si(111)-(7 × 7) surface. The 2,5-positions of the thiophene molecule are di- σ bonded to an adjacent adatom–rest atom pair.

loss at 2324 cm⁻¹, which is associated with the C(sp²)-D stretching vibration.¹⁹ In comparison, the spectrum of Figure 2b for monolayer deuterated thiophene shows loss features at 3048 and 2190 cm⁻¹. The C–D stretching is red-shifted about 131 cm⁻¹ upon chemisorption reaction, definitively indicating that the α -positions in thiophene are directly bonded to the surface active sites when thiophene molecules approach the Si(111)-(7 × 7) surface.

In summary, we have unambiguously demonstrated that the adjacent adatom and rest atom can serve as a diradical for the heterogeneous [4 + 2] cycloaddition reaction between thiophene molecules and the Si(111) surface. The resulting cycloadduct follows a 2,5-dihydrothiophene-like structure with the S-atom and the remaining C=C bond tilted from the surface, shown schematically in Figure 3.

The selective [4 + 2] cycloaddition of thiophene on Si(111)-(7 × 7) leads to the direct attachment of a functional C–S–C linkage onto the surface. This novel methodology can be extended to a wide range of useful heteroaromatics, such as furans and pyrroles, opening up new routes beyond those on Si(100) surfaces^{9–10,21} for further functionalization of the silicon surface.

Acknowledgment. We thank the financial support (RP3970612 and RP981644) of this work by National University of Singapore.

Supporting Information Available: Figure 4 and Tables 1 and 2 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA993386Q

(20) Additional vibrational losses at 1595, 1322, 1174, 1088, 925, 827, 754, and 565 cm⁻¹ are assigned to C=C stretching, C–H in-plane bending; C–C stretching, C–S–C stretching, C–H out-of-plane bending, and C–Si stretching modes, respectively.

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(17) The spacing between adjacent rest atom and adatom is 4.45 Å, which is quite comparable to the dimension of thiophene (~2.47 Å). Considering the formation of C–Si bond (~1.8–2.1 Å), a bridged geometry is reasonable.

(18) Our TDS results show three desorption peaks for thiophene adsorbed on Si(111)-(7 × 7) at 110 K. The multilayer thiophene and the first physisorbed state of thiophene desorb at 137 and 159 K, respectively. The stronger binding state of chemisorbed thiophene desorbs at 414 K.

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