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

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The binding of functional organic molecules onto solid substrates plays significant roles in developing advanced optics, microelectronics and sensors. It is possible to design and create organic/solid interfaces with chemical and biological functionalities by surface modifications. One modifier that offers promise for the improvement of the electron and energy transfer through the organic/inorganic interfaces is thiophene. Conjugated polythiophene and oligothiophene have recently been used as active layers by thin film deposition in electronic devices, such as field-effect transistors (FETs) and light-emitting diodes (LEDs). Layers by thin film deposition in electronic devices, such as field-effect transistors (FETs) and light-emitting diodes (LEDs). One modifier that offers promise for the improvement of the electron and energy transfer through the organic/inorganic interfaces is thiophene. Conjugated polythiophene and oligothiophene have recently been used as active layers by thin film deposition in electronic devices, such as field-effect transistors (FETs) and light-emitting diodes (LEDs). 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, where the covalent attachment of thiényls 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 deposition. The annealed silicon (111) surface is (7 × 7)-reconstructed, which presents a rich array of electronically inequivalent reaction sites, providing opportunities to explore the nature of local environments on the surface chemical reactivities. 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 dimerized Si(100)−(2 × 1) surface, where the “Si=Si” dimers can undergo cycloaddition reactions with butadienes in analogy of “C=C”. In a recent study of 1,3-dienes adsorption on Si(100), using STM and FTIR, 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, respectively. The unique geometric and electronic features of the adjacent rest atom−adatom pair (see Figure 1a) imply a “diradical” site for surface reaction. On the other hand, thiophene is documented as one of the least reactive dienes in solution cycloaddition reaction due to its high aromaticity. 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. Thiophene has a high π-electron density. In addition, the electron

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, Vm = 1.7 V, Im = 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.

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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. 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 μA·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. 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 normal. The scattered electrons were detected at the specular direction. The resolution of the spectrometer (linewidth of the elastic peak) is ∼5–6 mV.

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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.

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Figure 2. HREEL spectra for monolayer and multilayer thiophene on Si(111)−(7 × 7). (a) monolayer thiophene, (b) monolayer 2,5-dz-thiophene, (c) multilayer thiophene (3.0 L), and (d) multilayer 2,5-dz-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 (linewidth 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-α bonded to an adjacent adatom—rest atom pair.

loss at 2324 cm⁻¹, which is associated with the C(sp³)−D stretching vibration. 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.

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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