

Self-Induced 1-D Molecular Chain Growth of Thiophene on Ge(100)

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The fabrication and application of well-ordered, single-phase hybrid structures of organic molecules on semiconductor (100) surfaces, such as Si, Ge, and C (diamond) surfaces, have received particular attention. They offer the possibility of incorporating organic molecules into existing semiconductor-based microelectronic technologies. Many research groups have attempted to fabricate highly ordered molecular structures on semiconductor (100) surfaces using cycloaddition^{1a,b} or Lewis acid–base^{1c} reactions; however, because organic molecules can typically adsorb onto these surfaces with various geometries, highly ordered structures have only been achieved in a few cases.^{1a,c}

A heteroaromatic thiophene molecule contains a sulfur atom and an aromatic ring; thus, it can adsorb on semiconductor (100) surfaces in a variety of ways, such as via a [4 + 2] cycloaddition reaction, a [2 + 2] cycloaddition reaction, and a Lewis acid–base reaction.

In the present study, we have studied the adsorption structures of thiophene on Ge(100) using scanning tunneling microscopy (STM), high-resolution core-level photoemission spectroscopy (HRPES) using synchrotron radiation, and density functional theory (DFT) calculations. Our results show that when thiophene molecules adsorb on a Ge(100) surface they preferentially form one-dimensional molecular chains with Ge–S dative bonding configurations via the Lewis acid–base reaction.

Figure 1a–d show filled-state STM images of thiophene on Ge(100) at room temperature after exposing the surface to 0.1, 2, 10, and 50 L of thiophene, respectively. When a clean Ge(100) surface is exposed to 0.1 L of thiophene (Figure 1a), the thiophene molecules preferentially form one-dimensional molecular chains (feature A). To examine the coverage dependence, we exposed a clean Ge(100) surface to 2 L of thiophene (Figure 1b). Figure 1b reveals that the growth of molecular chains is initiated at random sites and continues until the chains meet other chains located at neighboring dimer rows. Interestingly, these chains are not observed on adjacent Ge dimer rows because of unfavorable steric hindrance between chains on neighboring rows (Figure 1c). This result strongly suggests that the saturation coverage of thiophene molecules on the Ge(100) surface is 0.25 ML. To see if other adsorption structures form at higher thiophene exposures, we increased the exposure of thiophene to 50 L (Figure 1d). The STM image of the resulting surface shows not only the chains on every second dimer row but also additional bright, round-shaped features (feature B) between the chains.

To clarify the exact positioning of feature A, we examined line profiles of the feature (Supporting Information Figure S1a,b). These profiles show that the bright protrusions of feature A are located between up-Ge atoms and adjacent down-Ge atoms on the same

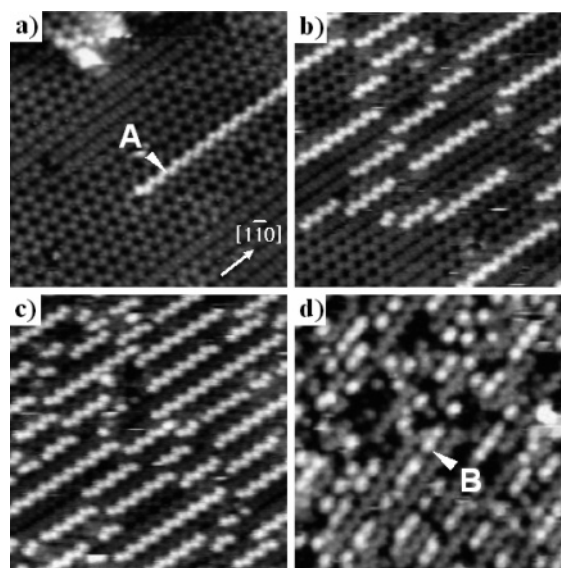


Figure 1. Filled-state STM images ($15 \times 15 \text{ nm}^2$, $V_s = -2.0 \text{ V}$, $I_t = 0.1 \text{ nA}$) of a Ge(100) surface when exposing (a) 0.1 L (0.02 ML), (b) 2 L (0.13 ML), (c) 10 L (0.21 ML), and (d) 50 L (0.26 ML) of thiophene.

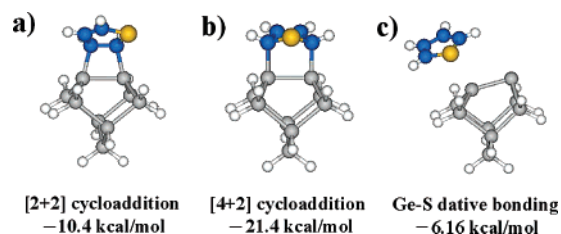


Figure 2. Local minima for $\text{C}_4\text{H}_4\text{S}/\text{Ge}_9\text{H}_{12}$ systems calculated at the B3LYP/LACVP** level of theory. The values are the adsorption energies with respect to free thiophene and Ge_9H_{12} .

side of the dimer row. The bright protrusions can be unequivocally assigned to thiophene molecules because they appear at the locations where there are no surface Ge atoms and because the aromatic ring of thiophene would be expected to image similarly to that of styrene^{1b} and pyridine,^{1c} both of which appear as bright protrusions in STM filled-state images. Analysis of the positions of feature B in comparison with the positions of the Ge dimers reveals that the protrusions are located on top of every second Ge dimer along the dimer row direction (Supporting Information Figure S1c,d).

To gain insight into the energetics of the possible reactions of thiophene on Ge(100), we performed DFT calculations on $\text{C}_4\text{H}_4\text{S}/\text{Ge}_9\text{H}_{12}$ systems, as shown in Figure 2. Similar to the previous theoretical results for thiophene on Si(100),² we found that the [4 + 2] cycloaddition reaction product is the most thermodynamically favorable. Additionally, the Ge–S dative bonding configuration was

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found to be the least stable structure from a thermodynamic viewpoint, although this reaction may have the lowest activation barrier, making it the most favorable from a kinetic viewpoint.

The sulfur atom in thiophene is sp^3 -hybridized, and therefore, the lone-pair electrons are tilted away from the aromatic ring plane. As a consequence, the ring plane of the adsorbed thiophene is tilted with respect to the surface when it is bound to Ge(100) via Ge–S dative bonding. Moreover, the C_2 axis of the thiophene ring has a dihedral angle of 105.5° to the Ge dimer bond. Thus, we expect that thiophene molecules may adsorb on down-Ge atoms with a “Gauche conformation” (Supporting Information Figure S2). This geometry is quite different from the adsorption geometry observed for the pyridine molecule in which the nitrogen atom is sp^2 -hybridized with in-plane lone-pair electrons.^{1c} Because the thiophene molecule adsorbs in the Gauche conformation in the dative bonding configuration, the ring of the thiophene molecule would be expected to be positioned above the location in the middle of adjacent Ge atoms along the dimer row direction, which is in good agreement with the positions of the protrusions of feature A in the STM image (Supporting Information Figure S1a).

As shown in Figure 1a–c, the [4 + 2] cycloaddition adduct is not formed at coverages under 0.25 ML. On a symmetric dimer, the [4 + 2] cycloaddition reaction proceeds with a very low activation energy along a symmetric reaction pathway; however, the most stable structure on Si(100) and Ge(100) surfaces at room temperature is the buckled dimer. Thus, for the [4 + 2] cycloaddition to proceed, it is necessary to overcome an activation energy equal to the energy difference between the buckled and symmetric dimers in addition to the energy barrier for bond formation via the [4 + 2] process. The ab initio first-principles calculations by Krüger and Pollmann indicate that the energy for buckled-symmetric flipping is 6.918 kcal/mol on Ge(100).^{3a} Therefore, the [4 + 2] cycloaddition of thiophene on Ge(100) is kinetically unfavorable compared to the Lewis acid–base reaction. Moreover, when thiophene molecules form molecular chains via Ge–S dative bonding, they may gain an additional stabilization energy due to the π – π stacking interaction.^{3b,c,4c} Thus, when thiophene molecules adsorb on Ge(100), they organize into molecular chains via dative bonding.

An adsorption of one thiophene molecule causes pinning of the buckling of adjacent dimers, which produces electron-deficient down-Ge atoms. Electrostatic interactions between the down-Ge atoms and the lone-pair electrons of thiophene and the intermolecular interactions by the π – π stacking stabilization facilitate the subsequent adsorption of another thiophene molecule. This mechanism would explain why thiophene molecules preferentially adsorb on Ge(100) dimers to produce molecular chains even at low coverages. At the saturation coverage of thiophene on Ge(100), 0.25 ML, there are still bare Ge dimers between adjacent molecular chains. Therefore, we can expect that the coverages to greater than 0.25 ML thiophene would react with these bare Ge dimers via the [4 + 2] cycloaddition.

To understand the coverage-dependent nature of bonding of adsorbed thiophene on Ge(100), we investigated the S 2p core-level spectra of the adsorbed thiophene on a Ge(100) surface using synchrotron radiation as a function of thiophene exposure. Figure 3a displays the S 2p core-level peaks after exposing a clean Ge(100) surface to 25 L of thiophene at room temperature. We can resolve these spectra into two bonding features, one located at 162.7 eV (marked as A) and the other at 161.8 eV (marked as B). Since the binding energy for physisorbed thiophene on a metal surface at low temperature is usually around 164 eV,^{4a–c} we can exclude the existence of the physisorbed thiophene. When the thiophene

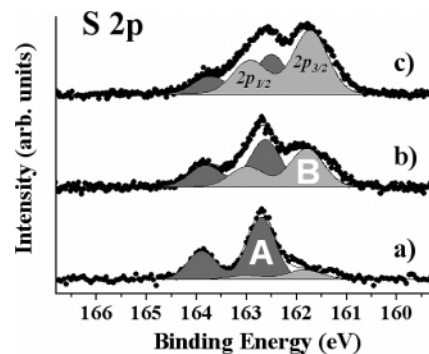


Figure 3. PES spectra in the S 2p region of the Ge(100) sample at thiophene exposures of (a) 25 L (84:16), (b) 50 L (52:48), and (c) 100 L (36:64) (values in parentheses correspond to area ratios). The dots are experimental values, and the solid lines represent the results of peak fitting.

molecule is bound to the Ge atom via the stronger chemical bonding, the S atom withdraws electrons from the less electronegative Ge atom more strongly than the case for the weak electrostatic interaction in the Ge–S dative bond. Therefore, we assign these two peaks to the dative bonding state (A) and the chemical bonding state (B), respectively. Comparison of the PES spectra for thiophene exposures of 25, 50, and 100 L (Figure 3a–c) clearly shows that the kinetically favored dative bonding configuration is the major component at low coverage, but that the ratio of the [4 + 2] cycloaddition adduct to the dative bonding configuration gradually increases with increasing thiophene exposure. This behavior is consistent with the STM results.

In summary, our results show that thiophene molecules adsorb on a Ge(100) surface at room temperature with two distinct geometries. At thiophene coverages under 0.25 ML, the kinetically favored Ge–S dative bonding configurations are observed and organized as one-dimensional molecular chains. At coverages over 0.25 ML, however, the thermodynamically stable [4 + 2] cycloaddition adducts are observed between the molecular chains of Ge–S dative bonding configurations. The tendency of thiophene to form molecular chains on Ge(100) could potentially be exploited in molecular device and lithography applications.

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Supporting Information Available: Experimental details, STM images, and density functional calculations (DFT) are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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