Electronic structures of thiophene on Ge(100): the roles of coverage and temperature

# Electronic structures of thiophene on Ge(100): the roles of coverage and temperature

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## Abstract
We investigated the adsorption and decomposition of thiophene ($C_4H_4S$) on Ge(100) using high-resolution photoemission spectroscopy. We found that the Ge 3d and C 1s core-level spectra revealed three adsorption geometries, which we assigned to a weakly bound state (i.e., a Ge–S dative bonding state), a [4 + 2] cycloaddition bonding state, and a decomposed bonding state (a desulfurization reaction product) as functions of the molecular coverage and the annealing temperature. In this study, we systematically elucidated the changes occurring in the bonding states of thiophene species adsorbed on a Ge(100) substrate.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Recently, the adsorption of organic molecules containing heteroatoms (such as S, O, and N) on semiconductor (100) surfaces has attracted much attention, not only from a fundamental viewpoint but also because of the potential industrial applications [1–5]. Well-ordered hetero-organic molecular layers have been prepared on semiconductor surfaces, usually by means of cycloadditive [6, 7] or Lewis acid–base [8] reactions between the organic molecules and the semiconductor surface dimers.

Polythiophene and its derivatives are particularly interesting because of their versatile applications, which include the fabrication of electroluminescence displays and optoelectronic devices (color-switching and memory), the protection of semiconductors against photocorrosion, and energy storage [9–11]. Thiophene—the building block of polythiophene derivatives—is composed of a sulfur atom and a conjugated diene, which induces a variety of surface reactions with semiconductor (100) surface atoms.

Recent studies have shown that it is possible to achieve a stable interface between thiophene and Si(100) by means of a [4 + 2] Diels–Alder cycloaddition in which the dienes of the thiophene species react with the Si(100) dimers acting as dienophiles [12, 13]. In many surface reactions, the Ge(100)-2 × 1 surface dimers are expected to have a surface reactivity similar to that of Si(100). However, due to the slight dissimilarities in the geometric and electronic structures, thiophene molecules may show quite different reactivities on the two semiconductors. In a previous study, we found that thiophene molecules initially formed one-dimensional molecular-chain structures, thereby exhibiting various adsorption geometries which varied with the coverage and the annealing temperature. The study was performed by using STM image analysis, S 2p photoemission spectroscopy, and DFT calculations [14, 15]. However, no systematic studies in which the Ge 3d and C 1s core-level photoemission spectra are simultaneously analyzed have been conducted so far on the thiophene/Ge(100) system. Hence, to obtain more information about the variations in the adsorption geometries of the adsorbed thiophene species as a function of coverage and annealing temperature, we performed photoemission studies of the Ge 3d and C 1s core-level spectra.

In this study, we investigate the changes occurring in the adsorption and decomposition sites of thiophene molecules on Ge(100) as we track the variations observed in the Ge 3d and C 1s core-level peaks (under various conditions) by using high-resolution photoemission spectroscopy (HRPES).

## 2. Experiment

The Ge(100) sample (p-type, $R = 0.10$–$0.39$ $\Omega$) was cleaned by means of several sputtering cycles using 1 keV Ar$^+$ ions (20 min, 700 K) followed by annealing at 900 K (for 10 min). The cleanliness of the Ge(100)-2 $\times$ 1 surface was checked by using low-energy electron diffraction (LEED). Thiophene ($C_4H_4S$, 99% purity) was purified by means of several freeze–pump–thaw cycles to remove any dissolved gases prior to its exposure to the Ge(100) surface. High-resolution core-level photoemission spectra were taken using a soft x-ray beamline (3A1) at the Pohang Accelerator Laboratory. The Ge 3d and C 1s core-level spectra were obtained with a high-performance electron analyzer (SES-2002, Gamma Data, Sweden) using photon energies of 100 and 500 eV, respectively. The overall resolution was 0.03 eV for the Ge 3d spectrum and 0.10 eV for the C 1s spectrum. The binding energies of the core-level spectra were referenced to the valence band (Fermi energy) of an Au foil at the same photon energy. The base pressure of the chamber was maintained at $7.0 \times 10^{-11}$ Torr. All the spectra were recorded in the normal emission mode, and the photoemission spectra were carefully analyzed by using a standard nonlinear least squares fitting procedure based on Voigt functions [16].

## 3. Data and results

Figure 1 illustrates four possible adsorption geometries for thiophene on a Ge(100) surface based on earlier studies on both Ge(100) [14, 15] and Si(100) [12, 13]. Figure 1(a) shows a weakly bound state in which the lone-pair electrons of the thiophene molecule are donated to the electron-deficient down atom of a Ge dimer via Ge–S dative bonding. A similar weakly bound state was also suggested by Lu *et al* for thiophene on Si(100) based on theoretically calculated local minima and transition states [13]. The authors concluded that the Si–S bonding is so weak that the bonding state can be described as a physisorption state. By analogy, we also expect the Ge–S bonding to be a weak charge interaction, without any strong chemical bonding, which may be formed at low temperatures and coverages, thus being kinetically favored. Figure 1(b) shows a [2+2] cycloaddition bonding state. A similar bonding state for the adsorption of thiophene on Si(100) was initially proposed by Jeong *et al* [17]. However, recent studies [12, 13] contradict this proposal and suggest the formation of 2,5-dihydrothiophene-like species based on a [4+2] cycloaddition reaction. On the basis of previous reports [13, 15] regarding the adsorption of thiophene on Ge(100), we can also exclude the possibility of the formation of a [2 + 2] cycloaddition adduct. Figure 1(c) shows the well-known [4+2] cycloaddition bonding state which is characterized by a strong chemical bond between the two $\alpha$-carbons of a thiophene molecule and the
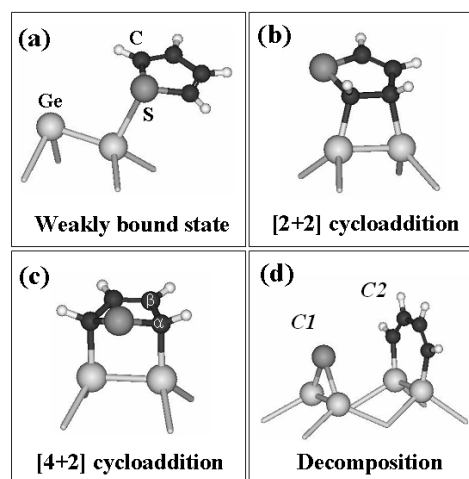


**Figure 1.** Schematic models for: (a) a weakly bound state, (b) a [2 + 2] cycloaddition bonding state, (c) a [4 + 2] cycloaddition bonding state, and (d) a decomposed bonding state.

two Ge atoms of a Ge(100) dimer. In this case, we predict that this bonding state is thermodynamically more stable than the weakly bound state. Finally, figure 1(d) shows the decomposed bonding state, which can be produced by desulfurization of the [4 + 2] adduct via S-atom migration to a neighboring Ge dimer to form germanium sulfide (C1:Ge$_2$S) and a metallocyclic compound (C2:C$_4$H$_4$Ge$_2$).

On the basis of this information on the adsorption and decomposition of thiophene on Ge(100), we performed HRPES studies at various thiophene coverages and annealing temperatures in order to understand the effects of these two parameters on the bonding character of the adsorbed thiophene molecules.

Figure 2(a) shows the Ge 3d core-level spectrum obtained for on a clean Ge(100) surface. The spectrum is resolved into three well-defined features [18], which can be assigned to bulk Ge atoms (29.2 eV), subsurface Ge atoms (29.0 eV, marked as S$'$), and up atoms of asymmetric Ge dimers (28.7 eV, marked as S). After confirming the cleanness of the Ge(100) surface, we exposed it to varying amounts of thiophene at room temperature. Figure 2(b) shows the Ge 3d core-level spectrum taken after exposing the semiconductor surface to 25 L of thiophene at room temperature. As can be seen, this spectrum is remarkably different from that obtained for on clean Ge(100). First, the exposure of the semiconductor surface to thiophene molecules leads to an attenuation of the surface states (S) as a result of the reconstruction and redistribution of the electron densities of the Ge atoms at the surface (caused by adsorbate–substrate interactions). Moreover, the intensity of the subsurface peak (S$'$) decreases after thiophene adsorption. Second, we observed the emergence of a new low-intensity peak (marked as A$'$, green color) which was located 0.18 eV higher than the bulk Ge 3d peak (29.2 eV). We believe that this feature arises from a small amount of thiophene found in the weakly bound state (see figure 1(a)).

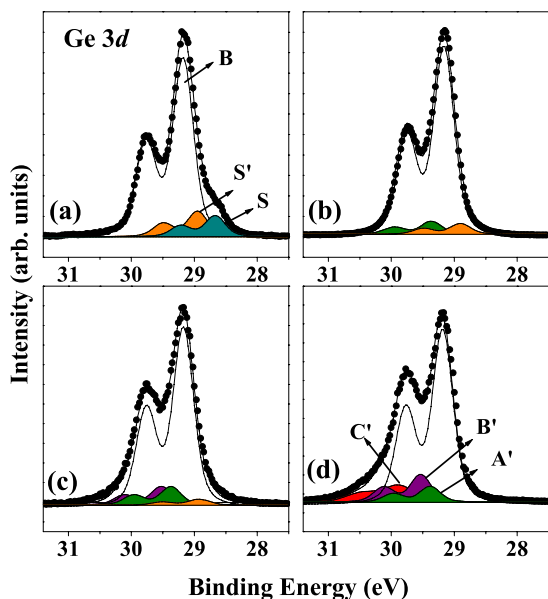To examine the changes in intensity among the different bonding features as a function of thiophene coverage, we

**Figure 2.** Ge 3d core-level spectra of the clean Ge(100) surface (a), and of the surface covered with: (b) 25, (c) 50, and (d) 200 layers (L) of thiophene. The photon energies were taken at $h\nu = 100$ eV. The dots are experimental values and the solid lines represent the results of peak fitting.



**Figure 3.** C 1s core-level spectra of the clean Ge(100) surface (a), and of the surface covered with: (b) 25, (c) 50, and (d) 200 L of thiophene. The photon energies were taken at $h\nu = 500$ eV (C 1s). The dots are experimental values and the solid lines represent the results of peak fitting.

recorded core-level spectra at higher thiophene exposures. Figure 2(c) shows the Ge 3d core-level spectrum obtained after exposing the semiconductor surface to 50 L of thiophene at room temperature. We found a new peak (marked as B′, purple color), with a binding energy of 29.53 eV (which is evident from the higher-binding-energy tail). Considering this shift to higher binding energies, we believe that this new feature may correspond to a more strongly bonded state. Thus, we regard this feature as arising from a [4 + 2] cycloaddition bonding state, between the Ge(100) dimer and two $\alpha$-carbons (see figure 1(c)). Additionally, the intensity of the peak corresponding to the Ge subsurface state (i.e., S′) decreases with increasing thiophene coverage. To clarify the variations in the two bonding states as a function of thiophene coverage—and to confirm whether any other features emerge—we additionally conducted experiments in which a clean Ge(100) surface was exposed to up to 200 L of thiophene. The corresponding Ge 3d core-level spectrum is shown in figure 2(d). As can be seen, the spectrum changes markedly on going from 50 to 200 thiophene layers. Specifically, the subsurface feature (S′) fully disappears while a new bonding feature (marked as C′, red color) appears. The new feature has a binding energy of 29.88 eV, which is 0.68 eV higher than that of the bulk peak. On the basis of previously reported values for the binding energy shift of $Ge_2S$ with respect to the bulk peak (i.e., 0.66 [19] and 0.67 eV [20], which are similar to the shift of 0.68 eV observed here for the C′ bonding feature), we can assign this feature to a strong bonding state, between a Ge(100) dimer and a sulfur atom. Thus, we believe that the sulfur atom of the thiophene molecule directly combines with Ge(100) surface atoms through a desulfurization reaction, as shown in figure 1(d).
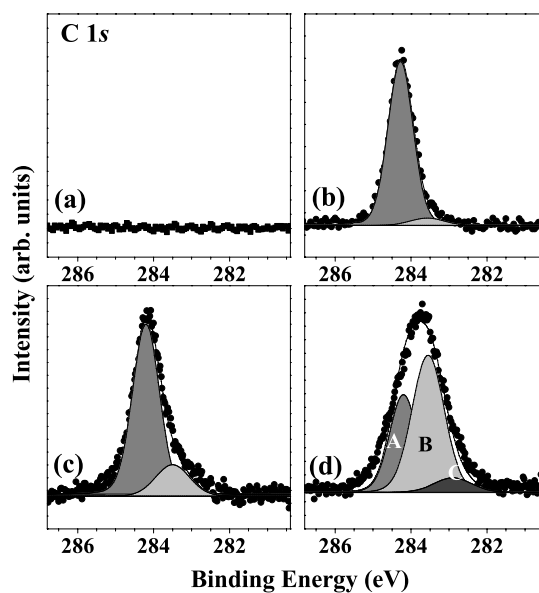
We simultaneously obtained a background C 1s core-level spectrum to confirm that the Ge(100) surface was clean. Figure 3(a) does not show any spectral features, thus indicating that no impurities or residual gases were present. Figure 3(b) shows the corresponding spectrum for the 25 L thiophene system, which can be resolved into two components found at 284.27 and 283.54 eV. These bonding features can be assigned to the weakly bound state and the [4+2] cycloaddition bonding state, respectively. We can conclude that the weakly bound state dominates at this coverage (as confirmed by the core-level peaks of Ge 3d and C 1s). Figure 3(c) shows a C 1s core-level spectrum recorded after exposing the Ge(100) surface to 50 L of thiophene at room temperature. A comparison of this spectrum with that obtained at 25 L (see figure 3(b)) discloses that the intensity of the [4+2] cycloaddition bonding feature is enhanced (relative to that of the weakly bound state) when the amount of thiophene is increased from 25 to 50 L, although the intensity of the weakly bound state is still larger at this coverage. To precisely delineate the changes for each component, we examined the C 1s core-level spectrum after exposing the germanium surface to 200 L of thiophene (see figure 3(d)). In this spectrum, we could clearly identify a new bonding peak (marked as C) located at 282.89 eV (C 1s). We believe that this peak corresponds to the decomposed bonding state, although the peak for this state has the smallest intensity among all three adsorbed bonding features.

Spectral analysis at room temperature indicates that three bonding states (namely, the weakly bound state, the [4 + 2] cycloaddition bonding state, and the decomposed bonding state) coexist at all the thiophene coverages studied, although the relative number of thiophene molecules present in each state varies as a function of the exposure. The weakly bound state dominates at a thiophene exposure of up to 25 L, thus
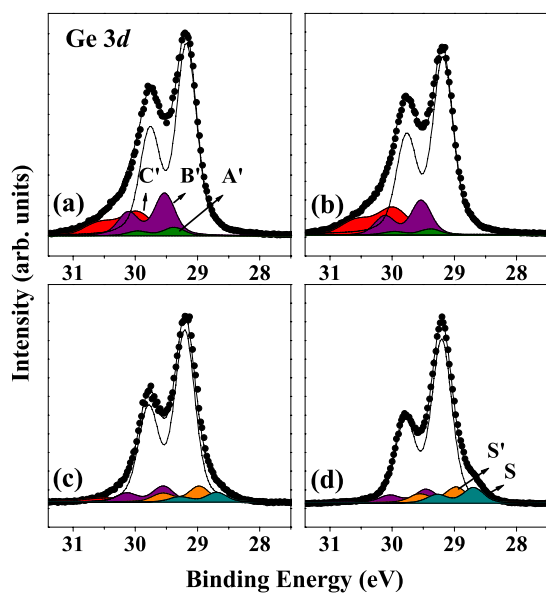
**Figure 4.** Core-level spectra for thiophene (200 L) on Ge(100) (the substrate was first exposed to thiophene at room temperature and then subjected to annealing at a higher temperature). The Ge 3d core-level spectra were taken after annealing for 5 min at: (a) 430, (b) 500, (c) 570, and (d) 670 K. The photon energies were taken at $h\nu = 100$ eV (Ge 3d). The dots are experimental values and the solid lines represent the results of peak fitting.
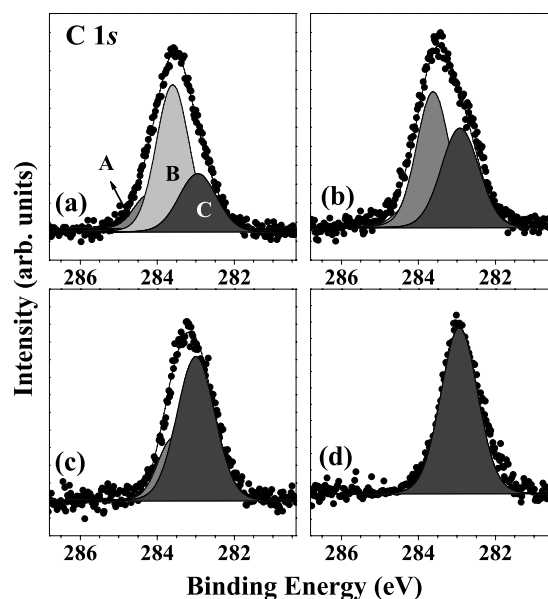


**Figure 5.** Core-level spectra for thiophene on Ge(100) systems that were exposed to 200 L thiophene at room temperature and then subjected to annealing at higher temperature. C 1s core-level spectra were taken after annealing for 5 min at 430 K (a), at 500 K (b), at 570 K (c), and at 670 K (d). The photon energies were taken at $h\nu = 500$ eV (C 1s). The dots are experimental values and the solid lines represent the results of peak fitting.

**Table 1.** Curve fitting results for the predicted structures shown in figure 1.

| Component | Predicted geometry | $E_B$ (eV) | |
|---|---|---|---|
| | | C 1s | Ge 3d |
| A | Dative bonding | 284.27 | 29.38 (A′) |
| B | [4 + 2] cycloaddition | 283.54 | 29.53 (B′) |
| C | Decomposition | 282.89 | 29.88 (C′) |

indicating that this state is kinetically favored, whereas the proportion of molecules in the [4 + 2] cycloaddition bonding state starts to increase at a thiophene exposure of 50 L. A further coverage increase (to 200 L) leads to the appearance of the decomposed bonding state. The binding energies of each component are summarized in table 1.

To monitor the changes among the three different bonding features as a function of the annealing temperature, we obtained a series of Ge 3d and C 1s core-level spectra for Ge(100) surfaces that were first exposed to 200 L of thiophene (at room temperature) and then annealed for 5 min at various temperatures.

First, we found that the intensities of both the Ge–C (marked as B′) and the Ge–S (marked as C′) bonding features in the Ge 3d core-level spectrum (see figure 4(a)) were greater after annealing at 430 K. On the other hand, annealing leads to a decrease in the intensity of the feature associated with the weakly bound state (marked as A′), because the higher temperature promotes desorption of molecular thiophene or cycloaddition to form more stable [4+2] products. Figure 4(b) shows the Ge 3d core-level spectrum recorded after annealing at 500 K. The intensities of the two bonding features B′ and C′ are greater in this case than in the corresponding spectrum

at 430 K (see figure 4(a)), and the feature associated with the weakly bound state (A′) has almost disappeared. Moreover, the intensity of the Ge–S (C′) bonding state is greater than that of the Ge–C (B′) state. After annealing at 570 K, we found that the feature associated with the weakly bound state in the Ge 3d core-level spectrum fully disappeared while the other two features (i.e., Ge–C: B′ and Ge–S: C′) decreased remarkably (see figure 4(c)). In particular, the Ge–S bonding feature was found to exhibit a very low intensity. Interestingly, two surface states that had disappeared after the adsorption of thiophene onto the semiconductor surface are recovered upon annealing at 570 K. Finally, we consider the effect of annealing at 670 K (see figure 4(d)), which is known to be a temperature of germanium sulfide desorption [20, 21]. In the Ge 3d core-level spectrum (figure 4(d)), the Ge–S (C′) bonding feature has fully disappeared (desorption), and the intensities of the two surface states are enhanced compared to those of the spectrum taken at 570 K. On the other hand, the Ge–C (B′) bonding feature is still present, which indicates the existence of a strong bonding state, such as a metallocyclic compound, $C_4H_4Ge_2$, or carbide.

The same trend is clearly observed for the intensity changes in the C 1s core-level spectra. As shown in figure 5(a), the strong bonding features (namely, [4 + 2] cycloaddition (B) and decomposition (C)) increase, whereas the feature corresponding to the weakly bound state (A) increases markedly. These results indicate that the [4 + 2] cycloaddition and decomposed bonding states are thermodynamically favorable. However, in figure 5(b)—obtained after annealing at 500 K—the signal corresponding to the [4+2] cycloaddition bonding state shows a greater intensity than that of the
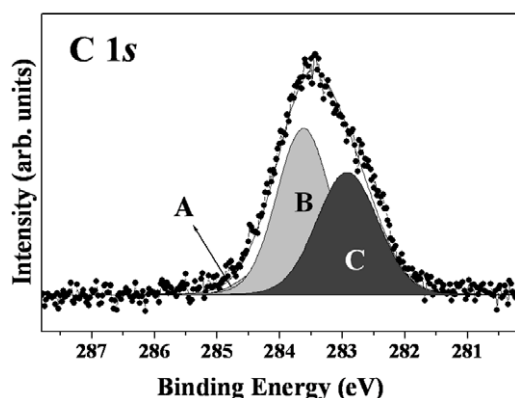
**Figure 6.** C 1s core-level spectrum of a Ge(100) sample exposed to 200 L of thiophene (at room temperature) and then annealed for 5 min at 500 K. A photon energy of $h\nu = 500$ eV was used. The dots are experimental values and the solid lines represent the results of peak fitting.

decomposed bonding state, which suggests that the [4 + 2] chemisorbed bonding feature still remains at this annealing temperature. In figure 5(c), the decomposed bonding state dominates whereas the [4 + 2] cycloaddition bonding state appears as a low-intensity signal. Finally, the C 1s core-level spectrum obtained after annealing at 670 K (see figure 5(d)) shows only a single feature, which corresponds to bonding between Ge and C. Because the binding energy of this latter peak is quite different from that of a Ge–C alloy [22], we can exclude the possibility of Ge carbide formation at this annealing temperature.

## 4. Discussion

Analysis of the C 1s core-level spectrum of a Ge(100) sample annealed at 500 K after exposure to 200 L of thiophene (see figure 6) reveals a clear discrepancy in the FWHM (full width at half-maximum) values of the C 1s components induced by the [4 + 2] adduct (B) and the decomposed thiophene species (C). The FWHM values of features B and C are 1.0 and 1.3 eV, respectively. This discrepancy indicates that the two features arise from carbon atoms in different chemical environments. One carbon atom directly bonds to a more electropositive Ge atom whereas the other one bonds to other carbon atoms. The observation of a larger FWHM for the decomposed bonding state than for the [4 + 2] cycloaddition bonding state can be attributed to the bonding character of sulfur. Specifically, in the [4 + 2] adduct (B), the more electronegative sulfur atom withdraws electrons from the $\alpha$-carbon (see figure 1(c)), thus lessening the decrease in the binding energy due to the electron-donating effect of the Ge atom. On the other hand, in the case of decomposed thiophene (C), the sulfur atom is not directly bound to the $\alpha$-carbon, so the electron-donating effect of the Ge atom acts only on the $\alpha$-carbon, thus resulting in a lower binding energy for the C (decomposition) components than for the B ([4 + 2] cycloaddition) ones. Moreover, due to electron–vibration coupling, the double-bond character ($-$C$=$C$-$) enhanced the

FWHM. Hence, the FWHM of feature C (Ge–C$=$C) is larger than that of feature B (S–Ge–C–C) [23].

## 5. Conclusion

The adsorption of thiophene at low coverages (i.e., 25 L) is dominated by a kinetically favored weakly bound state. Upon increasing the thiophene coverage to 50 L, we found that a thermodynamically stable [4 + 2] cycloaddition reaction takes over. By increasing the annealing temperature, we also confirmed that the kinetically favored adducts desorb first, followed by molecular desorption of the thermodynamically more stable [4 + 2] cycloaddition reaction products or by decomposition to form sulfur atoms and metallocyclic compounds. We expect this study of the electronic structures of thiophene on Ge(100) to be a good starting point for researching the electronic structures of polythiophene and its derivatives.

## Acknowledgments

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