Inter-row Adsorption Configuration and Stability of Threonine Adsorbed on the Ge(100) Surfaces

Myungjin Lee, Youngchan Park, Hyuk Jeong, and Hangil Lee*  
Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea. *E-mail: easyscan@sookmyung.ac.kr  
Received December 7, 2012, Accepted January 8, 2013

The adsorption structures of threonine on the Ge(100) surface were investigated using core-level photoemission spectroscopy (CLPES) in conjunction with density functional theory (DFT) calculations. CLPES measurements were performed to identify the experimentally preferred adsorption structure. The preferred structure indicated the relative reactivities of the carboxyl and hydroxymethyl groups as electron donors to the Ge(100) surface during adsorption. The core-level C 1s, N 1s, and O 1s CLPES spectra indicated that the carboxyl oxygen competed more strongly with the hydroxymethyl oxygen during the adsorption reaction. Three among six possible adsorption structures were identified as energetically favorable using DFT calculation methods that considered the inter- and intra-bonding configurations upon adsorption onto the Ge(100) surface. These structures were O-H dissociated N dative inter bonding, O-H dissociated N dative intra bonding, O-H dissociation bonding. One of the adsorption structures: O-H dissociated N dative-inter bonding was predicted to be stable in light of the transition state energies. We thus confirmed that the most favorable adsorption structure is the O-H dissociated N dative-inter bonding structure using CLPES and DFT calculation.

Key Words : Threonine, Ge(100), Inter-row adsorption configuration, DFT calculation, CLPES

Introduction

Studies of the reactions between organic molecules and semiconductor surfaces have become increasingly important over the past few years. Technologies that rely on interactions between organic materials and semiconductor technologies are being developed for molecular electronics, biosensor, and nanotechnology applications.1-8 An understanding of the reactions of amino acids, which act as zwitterions, on semiconductor surfaces may guide the design of these new technologies.9-11 Studies in this field have focused primarily on the covalent attachment of organics to group IV semiconductors.12 Methods for providing appropriate chemical functionalization of group IV semiconductor materials have been actively pursued.13-16

Our group has studied the adsorption structures and properties of a variety of amino acids on the Ge(100) surfaces in an effort to lay the groundwork for fabricating new bio-electronic hybrid devices.17-21 In this study, we have investigated the adsorption structures of threonine on the Ge(100) surface using core-level photoemission spectroscopy (CLPES) experiments and density functional theory (DFT) calculations. Threonine is a model molecule for studying the effects of multiple functional groups on the adsorption chemistry at a semiconductor surface. Threonine includes 4 carbon atoms bonded to a carboxyl group (-COOH), a hydroxyl group (-OH), an amine group (-NH₂), a methyl group (-CH₃), and a hydrogen atom.22-25 Several adsorption structures are possible for threonine on the Ge(100) surface, making threonine a very interesting adsorption test case.

We previously reported the adsorption structures of serine on the Ge(100) surface, which is structurally similar to threonine, with the exception of the side chain length. Serine was predicted to adsorb to the Ge(100) surface via a stable O-H dissociated N dative bonding.26 The similarities of threonine and serine suggest that the compounds should yield similar experimental and theoretical results. However, previous studies of serine did not consider the selectivity and stability associated with inter bonding and intra bonding. It is, therefore, necessary to examine the selectivity and stability of the threonine inter bonding and intra bonding adsorption structures to evaluate the possibility that threonine can interact with adjacent the Ge(100) surface dimers due to its chain length.

The primary purpose of this study was to investigate the competition between hydroxyl groups from hydroxymethyl and carboxyl groups during the adsorption of threonine on Ge(100). In addition, we also wanted to show the adsorption selectivity of inter bonding and intra bonding in the adsorption structure of threonine on the Ge(100) surface. The most stable adsorption configuration was identified, and the electronic structure was characterized experimentally using CLPES.

Scheme 1. Ball and stick model for chemical structure of 1-threonine. The blue, red, gray, and white colored balls indicate nitrogen (N), oxygen (O), carbon (C), hydrogen (H), respectively.
experiments and DFT calculations.

**Experimental Section**

The Ge(100) surface (p-type, $R = 0.10$-$0.39$ Ω) was cleaned using several cycles of sputtering with 1 keV Ar$^+$ ions for 20 minutes at 700 K, followed by annealing at 900 K for 10 minutes. The cleanness of the Ge(100) surface was checked using low-energy electron diffraction (LEED) and the existence of surface state in Ge 3$d$ core level spectrum using CLPES. Threonine (HO$_2$CCH(NH$_2$)CHOHCH$_3$, 99% purity) was purchased from Aldrich and further purified through several sublimation and pumping cycles to remove all dissolved gases prior to exposure to the Ge(100) surface. We defined 1.0 monolayer (ML) threonine coverage as the maximum density of threonine that could be deposited on the Ge(100) surface without yielding the N 1$s$ CLPES peak characteristic of multilayer formation.

CLPES experiments were performed at the 10D beamline of the Pohang Accelerator Laboratory. The C 1$s$, N 1$s$, and O 1$s$ core-level spectra were obtained using a PHOIBOS 150 electron energy analyzer equipped with a two-dimensional charge-coupled device (2D CCD) detector (Specs GmbH) using photon energies of 345, 460, and 600 eV to enhance the surface sensitivity. Four binding energies in the core-level spectra were calibrated with respect to the binding energy of a clean Au 4$f$ core-level spectrum (84.0 eV) at the same photon energy. The base pressure of the chamber was maintained below $9.5 \times 10^{-11}$ Torr. All spectra were recorded in the normal emission mode. The core-level spectra were carefully analyzed using a standard nonlinear least squares fitting procedure with Voigt functions.

DFT calculations were used to predict the energetics of the reaction pathways for threonine adsorption onto the Ge(100). All DFT calculations of the adsorption energies were performed using the JAGUAR 9.1 software package, which applied a hybrid density functional method and included Becke’s three-parameter nonlocal-exchange functional with the Lee–Yang–Parr (B3LYP) correlation functional. The calculations considered a four-dimer (Ge$_5$H$_3$) cluster models. The geometries corresponding to the important local minima on the potential energy surface were determined at the B3LYP/LACVP** level of theory. The LACVP** basis set is a mixed basis set that uses the LACVP basis set to describe Ge atoms and the 6-31G basis set for the remaining atoms. Moreover, the LACVP basis set describes atoms beyond Ar in the periodic table using the Los Alamos effective core potentials developed by Hay and Wadt. For each cluster, optimization was performed by fixing the bottom two layers of the Ge atoms in ideal Ge crystal positions while allowing the top layer of the Ge atoms (including the dimer atoms) and the atoms of the chemisorbed adsorbate to relax. The geometries of important local minima and the transition states on each energy diagram were also calculated. The local minima and transition states were verified as being optimized structures using the same basis sets.

**Results and Discussion**

CLPES data were acquired for the core-levels in a threo-

![Figure 1. C 1$s$ and O 1$s$ core-level spectra for (a, d) 0.15 ML, (b, e) 0.60 ML, (c, f) 0.85 ML threonine on the Ge(100) at 300 K. The dots indicate the experimental values and the solid lines represent the results of peak fitting.](image-url)
nine molecule adsorbed on the Ge(100) surface. Figure 1 shows a series of C 1s and O 1s core-level spectra as a function of the threonine coverage. We determined the C 1s core-level spectra for three distinct threonine coverage levels (0.15 ML, 0.60 ML, 0.85 ML) to corroborate our DFT calculation results.

Figure 1(a) shows the C 1s core-level spectrum obtained after the formation of a sample with 0.15 ML threonine at 300 K. The spectrum included four distinct bonding features corresponding to the four carbons of threonine in different chemical environments. Considering the relationship between electronegativity and binding energy, we assigned the bonding features C1, C2, C3, and C4 to -CH$_2$ (284.6 eV), C-NH$_2$ (285.3 eV), CH$_2$-OH (286.6 eV), and a deprotonated carboxyl carbon, -COO (287.7 eV), respectively. Increasing the coverage of threonine to 0.60 ML (Figure 1(b): more than half of a monolayer) produced features that differed from those found at 0.15 ML. A new peak (marked C2') emerged at 285.8 eV, indicating a change in the bonding structure due to the formation of a new adsorption structure. This observation suggested that the electronic state (or electric charge) of the amine group changed from positive to neutral. If the electric charge of the amine group became neutral upon formation of the adsorption structure, the electric charge of the amine group changed from positive to neutral. If the electric charge of the amine group changed from positive to neutral. If the electric charge of the amine group became neutral upon formation of the adsorption structure, the electric charge of the adjacent α-carbon should become more positive because of the reduced withdrawing ability of the neutral nitrogen atom. Therefore, the peak would be expected to shift toward higher binding energies. A further increase in the threonine coverage, beyond 0.85 ML, supported our definition of coverage. Figure 1(c) shows the C 1s core level spectrum obtained after deposition of 0.85 ML threonine. As expected, C2' peak was increased slightly. Intensity between C2' and C2 will precisely discuss at the N 1s core-level spectra (Fig. 2). The coverage-dependent variations in the adsorption structure for this system are, therefore, meaningful.

We next examined the variations in the O 1s peaks as a function of threonine deposition on the Ge(100) surfaces. Figure 1(d) shows the O 1s core-level spectrum obtained after deposition of 0.15 ML threonine. Considering the experimental resolution and the chemically inequivalent oxygen atoms in threonine, we divided the O 1s peaks into three components and assigned O1, O2, and O3, to O-Ge (530.3 eV), -C=O (531.3 eV), and -CH$_2$OH (532.8 eV), as in the serine system.

Based on the expected O 1s peak positions, the hydroxymethyl oxygen peak (-O$_m$H; where $O_m$ indicates the hydroxymethyl oxygen), typically located at 533.0 eV, should not have been observed if it were directly adsorbed onto the Ge(100) surface. Because the hydroxymethyl oxygen peak actually was observed, as shown in Figure 1(c), we could exclude the possibility that this atom was bonded to the Ge(100) surface in the adsorption structure. Therefore, the oxygen atom of the hydroxymethyl group did not participate in adsorption onto the Ge(100) surface.

Figure 2(a) shows a series of N 1s core level spectra as a function of the threonine coverage. Coverage-dependent variations of the adsorption structures are clearly observed for threonine on the Ge(100) surface. Below 0.50 ML, a single nitrogen bonding feature is present, whereas two types of nitrogen bonding features are observed at coverage levels beyond 0.50 ML. As in the C 1s core level spectra analysis, the coverage-dependent variations in the adsorption structure were observed based on the N 1s core level spectra.

Right panels of Figure 2 show the deconvoluted N 1s core level spectra for three distinct coverage levels in an effort to elucidate the variations based on the nitrogen bonding features of the three distinct coverage levels. Using the procedure described above, we obtained a deconvoluted N 1s core-level spectrum for 0.15 ML threonine (Figure 2(b)) adsorbed onto the Ge(100) surface at 300 K. The spectrum clearly contained a single N 1s peak (401.1 eV), which corresponded to the charged N atom in the threonine molecule. The peak (N1) assignments in previous studies involving N dative bonding adsorption structures on the Ge(100) surfaces clearly indicated that at lower coverage levels, the nitrogen atom in the amine group adsorbs onto the Ge(100) surfaces in a dative bonding configuration. Figure 2(c) shows the N 1s core-level spectrum obtained for a 0.60 ML coverage level, which corresponds to a distinct adsorption structure. This spectrum featured a new peak that emerged at 398.8 eV (marked N2), providing critical proof that a new adsorption structure was present at this coverage level. Based on our interpretation of the C 1s spectra, the new N 1s peak (N2) appeared to arise from positive-to-neutral changes in the
charge on the amine group. Thus, the nitrogen atom appeared to break its initial dative bonding with a Ge up-atom as the threonine coverage increased.

The intensity variations among the N 1s peaks shown in Figure 2(a), revealed an interesting property of the coverage-dependent variations in the adsorption structures of threonine on the Ge(100) surface. The appearance of a neutralized N bonding feature (marked N2) between 0.40 ML and 0.60 ML (Figure 2(a)), is clearly accompanied by a slight decrease in the intensity of the N dative bonding feature (marked N1). This change may be explained in terms of the structural properties at higher coverage levels: the N dative bonding feature transitions to a neutral N bonding feature.

The C 1s, N 1s, and O 1s core-level spectra demonstrated that the N1 peak arose from the O-H dissociated N dative bonding, and the N2 peak arose from O-H dissociation bonding. Furthermore, it was deduced that the O-H dissociated N dative bonding was dominant at low initial coverage levels whereas the O-H dissociation bonding emerged at higher coverage levels. The focus of this experiment was to clarify, using CLPES measurements, whether the hydroxymethyl oxygen or the carboxyl oxygen bound to the Ge(100) surfaces. We additionally sought to characterize the selectivity and stability of the inter bonding and intra bonding adsorption structures. This will be shown based on the DFT calculations.

We first proposed six possible adsorption structures for threonine on the Ge(100) surface to identify the most stable adsorption configuration, as shown in Figure 3. The adsorption structure corresponding to a high degree of selectivity between the inter bonding and intra bonding states was considered. This structure can potentially lead to O-H dissociated N dative intra bonding, O-H dissociated N dative inter bonding due to the long threonine chain length, which can facilitate binding to the adjacent dimer row on the Ge(100) surface.

The -OH group of the carboxyl group may also potentially be bound to the Ge(100) surface through O dative bonding (Fig. 3(a)), O-H dissociation bonding (Fig. 3(b)), O-H dissociated N dative inter bonding (Fig. 3(c)), and O-H dissociated N dative intra bonding (Fig. 3(d)). In addition to these four possible structures, we considered two structures involving the amine group on the adsorption process: N-H dissociation bonding (Fig. 3(e)), and O-H dissociated N dative intra bonding (Fig. 3(f)). Interestingly, the adsorption energies of the six possible adsorption structures predicted three stable adsorption structures on the Ge(100) surface.

Figure 4 shows the three most favorable adsorption structures (from among the six possible adsorption structures shown in Figure 3), viewed from the front and top and reported with the calculated adsorption energies. Two of the favorable adsorption structures were further evaluated, the O-H dissociated N dative inter-bonding structure and the O-H dissociated N dative intra bonding structure. The calculated adsorption energies suggested that O-H dissociated N dative inter bonding may characterize the dominant product because the calculated adsorption energy of this structure was the lowest ($E_{\text{ads}} = -69.51$ kcal/mol). On the other hand, O-H dissociated N dative intra bonding ($E_{\text{ads}} = -59.91$ kcal/mol) had relatively high adsorption energies compared with inter bonding adsorption structures.

A negligibly small difference in the adsorption energies of the two structures (O-H dissociated N dative inter bonding and O-H dissociated N dative intra bonding) supported possible adsorption structures. We next calculated the energies, transition states, and structures associated with each plausible reaction pathway for the two adsorption structures.

Figure 5 shows the reaction pathways for the formation of O-H dissociated N dative inter-bonding and O-H dissociated N dative intra-bonding. Figure 5(a) presents the reaction pathway for the O-H dissociated N dative inter-bonding, calculated from the initial O-H dissociation bonding. The value of transition state energy was $-43.09$ kcal/mol, which is thermodynamically stable. On the other hand, the theoreti-
chemically calculated adsorption pathway for the formation of the O-H dissociated N dative intra bonding structure, which includes a transition state with a positive structural energy (28.55 kcal/mol), is predicted to be thermodynamically unfavorable. Unlike the O-H dissociated N dative intra bonding structure, the transition state energies of the O-H dissociated N dative inter bonding structures were negative and their activation barriers was 7.77 kcal/mol, which may be easily overcome the reaction pathway at room temperature. Thus, this adsorption structure is predicted to be present on the Ge(100) surface during the initial phases of adsorption because its adsorption energy is calculated to be –69.51 kcal/mol, 9.60 kcal/mol lower than that of the O-H dissociated N dative inter bonding structure (E_{ads} = -59.91 kcal/mol).

**Conclusions**

We investigated the adsorption structures of threonine adsorbed onto the Ge(100) surface by performing CLPES experiments and DFT calculations. The analysis of the CLPES data, demonstrating that the O-H dissociated N dative bonding is preferred at low threonine coverage levels (0.15 ML). The core-level C 1s, N 1s, and O 1s CLPES spectra revealed that the carboxyl oxygen was more competitive than the hydroxymethyl oxygen in binding to the Ge(100) surface during adsorption. The O-H dissociated N dative bonding was preferred at low coverage levels (0.15 ML). DFT calculations of the adsorption energies allowed prediction of the three most energetically favorable adsorption structures among six possible structures. The three plausible structures include: O-H dissociated N dative inter bonding, O-H dissociated N dative intra bonding, O-H dissociation bonding. These structures are predicted to be relatively stable based on the calculated adsorption energy. The reaction pathways for achieving the energetically favorable adsorption geometries were modeled, showing that O-H dissociated N dative inter bonding pass through transition states with negative energies, suggesting that this is plausible reaction pathways. O-H dissociated N dative inter bonding yielded the most reasonable structure with the most stable energy (~69.51 kcal/mol). Finally, the CLPES experimental results, in combination with the DFT calculations of the transition states, demonstrated that the O-H dissociated N dative inter bonding reaction was more favorable than O-H dissociated N dative intra bonding at initial coverage.

**Acknowledgments.** This work was supported by the Sookmyung Women’s University Research Grants 2012.

**References**

24. Ramesh Kumar, G; Gokul Raj, S; Snakar, R; Mohan, R; Pandi, S; Jayaval, R. J. Crystal Growth 2004, 267, 213.