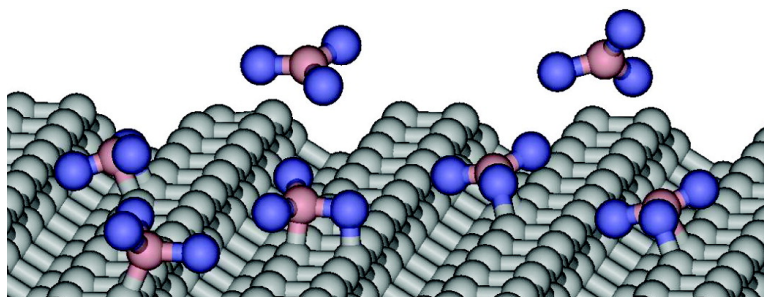


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Cycloaddition on Ge(100) of the Lewis Acid AlCl₃

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Recently, molecular adsorption on (100) surfaces of group IV elements has been intensively studied because of its various applications.¹ (100) surface dimers can react with unsaturated organic compounds in processes that are analogous to cycloaddition reactions in organic chemistry.² Furthermore, the reconstruction of the (100) surface results in the presence of electrophilic and nucleophilic sites,^{1c} and the surface atoms can thus participate in electron-transfer reactions such as Lewis acid–base reactions.³ Self-assembly techniques have recently been used to construct a one-dimensional heterogeneous molecular wire composed of two different organic molecules by making use of the electronic and structural properties of surface dimers.⁴ Hamers et al. reported that the adsorption of trimethylamine (a Lewis base) and BF₃ (a Lewis acid) on the Si(100) surface leads to the formation of a novel surface-mediated donor–acceptor complex with the structure TMA–Si–Si–BF₃.⁵ However, they did not discuss the adsorption structure of the acid molecule in detail.

The adsorption of Lewis base molecules with a lone pair of electrons on Ge(100) has been intensively studied.^{3a,b} In contrast, the adsorption of Lewis acid molecules on Ge(100) surfaces has not been studied at all. The study of the adsorption of Lewis acid molecules on Ge(100) surfaces will improve our understanding of how to design and construct selectively self-assembled nanostructures. Aluminum trichloride (AlCl₃) is a Lewis acid that forms donor–acceptor complexes with electron-rich molecules, so we focus on its reactions with the Ge(100) surface.

Figure 1a–c shows a series of filled-state ($V_s = -2.0$ V) scanning tunneling microscopy (STM) images recorded in real time for the same region of the Ge(100) surface during exposure to AlCl₃. The bright protrusion in the top center is a mark indicating that all the three images are of the same region of the surface. As can be seen in these images, there are three different adsorption features attributed to chemisorbed AlCl₃ molecules, labeled A, B, and C. In the enlarged STM images of these features in Figure 1d–f, feature A consists of two strong protrusions on one side of two adjacent dimers in the same dimer row and a depression on the other, feature B consists of two well-separated protrusions on the same dimer, and feature C contains a darker, round protrusion between two dimer rows. During the real-time STM experiments, we carefully investigated the changes in the structure of the Ge(100) surface during the adsorption of AlCl₃. Feature B (shown enclosed by a yellow box) in Figure 1a is converted to feature C (shown enclosed by a yellow dotted box) in Figure 1b (see the Supporting Information). A total of 3 min was required to obtain each STM image. When we compared a series of STM images obtained at 3 min intervals, we found that most B features were converted to C features. Note that all of the features in the filled-

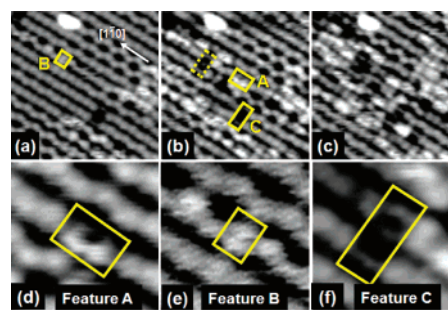


Figure 1. Filled-state STM images (7.6×7.6 nm², $V_s = -2.0$ V, $I_t = 0.1$ nA) of AlCl₃ adsorbed on a Ge(100) surface: (a) 0.01 monolayer (ML), (b) 0.2 ML, and (c) 0.4 ML. Enlarged STM images (2.5×2.5 nm², $V_s = -2.0$ V, $I_t = 0.1$ nA) of features A, B, and C are shown in (d), (e), and (f).

state STM images of AlCl₃ adsorbed on Ge(100) initially consist of two bright protrusions, which is quite different from the single protrusions found for dative bonded amine molecules.

Generally, amine molecules have three-fold symmetry, as is the case for AlCl₃. In contrast to AlCl₃, the adsorption configurations of amines are well studied.^{3a,b} The nitrogen lone pair of electrons of an amine can interact with an electrophilic “down” atom to form a dative bond. In the case of primary and secondary amines on a Si(100) surface, the complex in the adsorbed state can undergo N–H dissociation.^{3a} In the filled-state STM images of our system, however, the adsorbed AlCl₃ molecules appear as two protrusions in features A and B. Thus, we can exclude the presence of single dative bonds.

To clarify the electronic structure of AlCl₃ adsorbed on Ge(100), we used high-resolution core-level photoemission spectroscopy (HRCLPES). Figure 2a shows the Ge 3d core-level spectrum obtained for the clean Ge(100) surface, which can be resolved into three well-defined features.⁶ After confirming that the Ge(100) surface was clean in the Cl 2p core-level region (Figure 2d), we saturated the surface with AlCl₃. Exposure of the Ge(100) surface to AlCl₃ molecules leads to the attenuation of the surface state (S), possibly as a result of the redistribution of the electron density of the Ge atoms at the surface due to adsorbate–substrate interactions, and the subsurface peak (S′) decreases in intensity after AlCl₃ adsorption. Moreover, new peaks marked as A and A′ emerge at 0.2 and 0.6 eV higher, respectively, than the bulk Ge 3d peak (29.2 eV), indicating the presence of two different bonding states of Ge atoms. AlCl₃ contains three Cl atoms that are in equivalent chemical environments and one Al atom. When AlCl₃ attaches to a Ge surface dimer, the Pauling electronegativity (PE) difference between Ge (PE = 1.8) and Cl (PE = 3.0)⁷ is expected to move the Ge 3d peak to the higher binding energy region. Similarly, in previous studies of a Cl-terminated Ge surface, it has been reported that there is a chemical shift of the Ge 3d peak by 0.60 eV with respect

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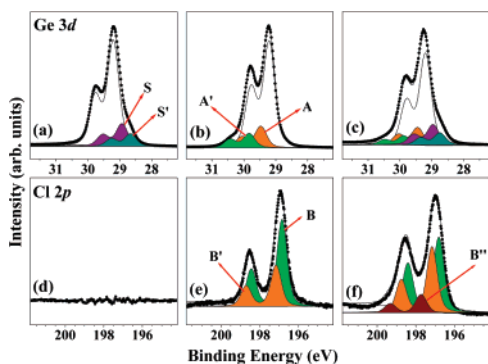


Figure 2. High-resolution core-level photoemission spectra of Ge 3d (upper panel) and Cl 2p (lower panel) for AlCl₃ adsorbed on Ge(100) at room temperature. (a,d) Core-level spectra of a clean Ge(100) surface. (b,e) Spectra of a Ge(100) surface saturated with AlCl₃. (c,f) Core-level spectra for AlCl₃ on Ge(100) surfaces exposed to 200 L AlCl₃ at room temperature and then subsequently annealed at 380 K. The photon energies were $h\nu = 100$ (Ge 3d) and 250 eV (Cl 2p). The dots are the experimental values, and the solid lines were obtained by peak-fitting.

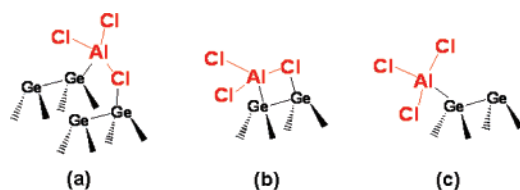


Figure 3. Adsorption structures of AlCl₃ on Ge(100).

to the bulk Ge 3d peak.⁸ Thus, we assigned the peaks at 29.4 and 29.8 eV to Ge–Al and Ge–Cl, respectively.

We also obtained the Cl 2p core-level spectrum of AlCl₃, shown in Figure 2e. The spectrum has two components with binding energies of 196.8 (B) and 197.2 eV (B'). As shown in Figure 2e, the area of the 196.8 eV peak is almost twice that of the 197.2 eV peak, indicating the presence of two distinct forms of Cl in a 2:1 ratio. Because Al (PE = 1.5) is a better electron donor than Ge (PE = 1.8),⁷ the bond between a Cl atom and an Al atom is normally expected to have a lower binding energy than the bond between a Cl atom and a Ge atom. Thus, B and B' are attributed to Cl atoms bonded to Al atoms and Cl atoms bonded to Ge atoms, which are more electronegative than Al atoms.

We annealed this sample at 380 K for an hour and investigated the resulting changes in electronic structure. As shown in Figure 2c, we found that the two peaks related to the surface states S and S' have reappeared, whereas the intensities of the peaks (A and A') related to adsorbed AlCl₃ states with binding energies 29.4 and 29.8 eV, respectively, have decreased significantly, which indicates that some AlCl₃ molecules have desorbed from the surface. The most significant effect of annealing observed in the Cl 2p spectrum (Figure 2f) is the appearance of a new Cl 2p peak (marked as B'') at a high binding energy (197.7 eV), which agrees with results for free Cl atoms adsorbed on the Ge surface⁸ and suggests that dissociation of Cl–Al bonds has occurred. From these results for the chemical shifts induced by annealing, Al–Cl bond breaking is expected to produce species such as Ge–AlCl₂ and Ge–Cl. The Ge 3d peaks at 29.4 and 29.8 eV, accompanied by the two distinct Cl 2p peaks at 196.8 and 197.2 eV, suggest that AlCl₃ molecules adsorb onto the Ge(100) surface and form Ge–Cl and Ge–Al bonds. Thus, feature A in Figure 1d is attributed to the structure in Figure 3a, and feature B in Figure 1e is attributed to the structure in Figure 3b. The structural strain that results from the tetragonal

configuration of AlCl₃ and the Ge dimer in Figure 3b leads to a transformation of the structure to that in Figure 3c, which corresponds to feature C in Figure 1f. Moreover, we have confirmed that the AlCl₃ molecules do not dissociate at room temperature, since there is no Cl 2p peak at 197.7 eV.

Interestingly, the adsorption structures of AlCl₃ on Ge(100) are quite different from those of NH₃ on Ge(100), for which a single dative bond forms, even though both molecules (AlCl₃ and NH₃) have three-fold symmetry. To determine the reason for this difference, we applied valence shell electron pair repulsion (VSEPR) theory. NH₃ has a pyramidal structure (C_{3v}) with a lone pair of electrons. In contrast, Al has only six electrons around it, and the AlCl₃ molecule has a planar structure (D_{3h} symmetry).^{9a,b} Aarset et al. concluded that the bonds in AlCl₃ have 20% double bond character from gas-phase electron diffraction results and *ab initio* molecular orbital calculations.^{9c} In the case of AlCl₃ on Ge(100), one Cl atom of AlCl₃ interacts with a “down” Ge atom when the Al atom interacts with an “up” Ge atom. In a typical cycloaddition reaction, the π bond between the alkene and the Ge–Ge dimer is broken and two new Ge–C σ bonds are formed in a bond arrangement referred to as a “di- σ bond”. The adsorption of AlCl₃ on Ge(100) also occurs by breaking two π bonds and forming a di- σ bond. Thus, AlCl₃ adsorbs on Ge(100) surfaces through a cycloaddition-like reaction.

In this study, we have elucidated the adsorption and electronic structures of AlCl₃ on Ge(100) by using STM and HRCLPES. We found that AlCl₃ molecules adsorb on the Ge(100) surface via a cycloaddition-like reaction and form di- σ bonds in which the AlCl₃ molecules interact with the surface dimers of Ge(100).

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Supporting Information Available: Experimental details and STM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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