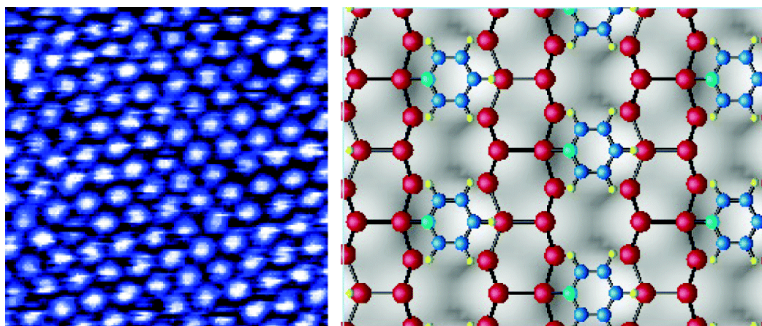


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Formation of Highly Ordered Organic Monolayers by Dative Bonding: Pyridine on Ge(100)

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Functionalization of semiconductor surfaces through chemisorption of organic molecules has generated much recent interest because of its potential applications in molecule-based devices, biosensors, nanolithography, and organic dielectrics.¹ The (100) surfaces of group IV elements (C(diamond), Si, Ge) are widely used as substrates for organic functionalization; these surfaces rearrange to form surface dimers whose bonding resembles the C=C bonds of alkenes. To date, cycloaddition has been the main reaction exploited to control the ordering of organic films on the surfaces of group IV elements.^{1,2} Hamers and co-workers produced highly ordered organic monolayers by utilizing cycloaddition between the double bonds of unsaturated organic molecules and the Si=Si dimers on a Si(100) surface.^{2c} However, previous studies have shown that a number of alkenes with more than one functional group (e.g., cyclohexadiene, cyclooctatetraene, etc.) do not adsorb onto (100) surfaces of group IV elements with a high degree of order, possibly due to the existence of various adsorption configurations and surface defects.³ Therefore, the problem remains of how to produce well-ordered monolayers of multifunctional molecules that bind to the surface by only one of their functional groups, leaving the other group available for subsequent layer attachment. Here, we present a novel route that gives highly oriented layers of N-containing organic molecules containing two functional groups, aromatic and amine groups. The key to this method is a Lewis acid–base reaction between the N atom in the molecule and the down-atom of the dimers on the Si(100) or Ge(100) surface.

Among the functional organic molecules studied to date, N-containing aromatic compounds such as pyrrole, pyridine, and aniline have generated particular interest because of their useful physical and chemical properties, deriving from their lone-pair electrons. Previous studies⁴ have suggested that aromatic amines such as pyrrole and aniline adsorb onto Si(100) via formation of a Si–N covalent bond with cleavage of the N–H bond. Pyridine is a tertiary amine with an aromatic ring. Theoretical and scanning tunneling microscopy (STM) studies⁵ of the adsorption of pyridine onto a Si(100) surface have shown that pyridine molecules adsorb molecularly onto the surface predominantly through Si–N dative bonding and that the resulting Si–N adsorption configuration is then gradually converted to a bridge-type configuration, similar to the case of benzene on Si(100).⁶

In the present study, the adsorption of pyridine onto the Ge(100) surface was investigated using STM and *ab initio* pseudo-potential density functional calculations. We find that pyridine molecules adsorb with very high order and selectivity onto Ge(100) via the formation of Ge–N dative bonds through a Lewis acid–base type reaction. The present results demonstrate that a Lewis

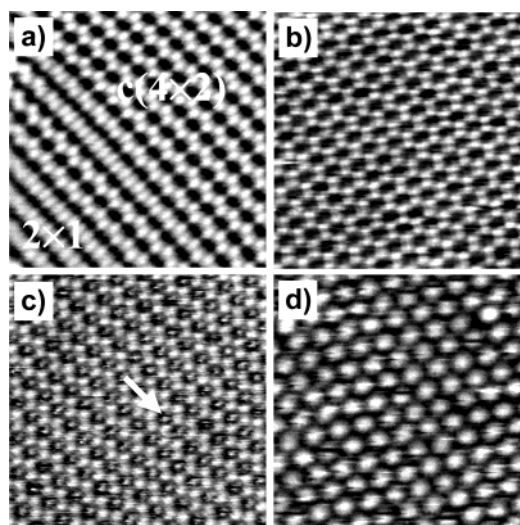


Figure 1. Sequence of filled-state STM images ($10 \times 10 \text{ nm}^2$, 0.1 nA) of (a) a clean Ge(100) surface (-1.8 V) and 0.25 ML of pyridine adsorbed onto the surface at bias voltages (V_s) of (b) -1.0 V , (c) -1.8 V , and (d) -2.4 V . The images show that the Ge substrate and adsorbed pyridine molecules can be identified by varying the sample bias voltages.

acid–base type reaction can be used as a novel scheme to form well-defined organic monolayers.

Figure 1a shows a filled-state STM image of the clean Ge(100) surface. The clean surface is almost defect-free and contains alternating asymmetrical $c(4 \times 2)$ and symmetric 2×1 domains, consistent with previous results.^{2f,7} Parts b–d of Figure 1 show filled-state STM images of the Ge(100) surface after adsorption of 0.25 ML of pyridine at room temperature for the same region recorded at sample bias voltages of $V_s = -1.0, -1.8, \text{ and } -2.4 \text{ V}$, respectively. The STM images of the adsorbed pyridine surfaces vary markedly with changing bias voltage. These bias-dependent STM images can be utilized to investigate the detailed adsorption geometry of pyridine molecules on Ge(100). The STM image recorded at a bias voltage of -1.0 V (Figure 1b) shows a uniform asymmetrical $c(4 \times 2)$ arrangement over the entire sample, indicating that the adsorption of pyridine induces buckling of the symmetrical Ge dimers on Ge(100). At $V_s = -1.8 \text{ V}$ (Figure 1c), however, both the pyridine molecules and the underlying substrate are imaged simultaneously. The image obtained at this bias voltage contains regularly arranged dot-like features (one of which is indicated with an arrow) located between the Ge dimer rows, slightly closer to one side of the dimer row. We assign these dot-like features to pyridine molecules adsorbed onto Ge(100). The uniform distribution of these features indicates that the pyridine

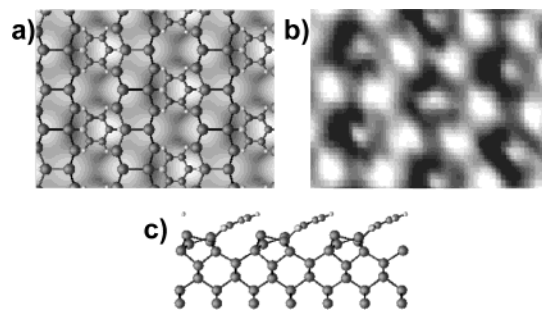


Figure 2. Comparison of (a) theoretically calculated (-1.8 V) and (b) experimental filled-state STM images (-1.8 V, 0.1 nA) of the Ge(100) surface at a pyridine coverage of 0.25 ML. (c) Side view of the optimized structure.

molecules have a single favored adsorption configuration. At the higher bias voltage of -2.4 V (Figure 1d), the STM image contains only a perfectly ordered array of round features with a densely packed structure, without the underlying substrate. The spacing between these features is identical to that of the dot-like features recorded at the bias voltage of -1.8 V and twice that between adjacent Ge dimers in the dimer rows of Ge(100). Thus, we assign these round features to pyridine molecules adsorbed possibly by a single configuration on Ge(100). The circular shape of the adsorbed pyridine molecules in the STM image may suggest that they are attached with the plane of the ring parallel to the surface. Compared to previous results for the adsorption of cyclopentene on Si(100),^{2c} the pyridine layer adsorbed on Ge(100) shows a higher degree of ordering.

A pyridine molecule with two different functional groups can be attached to the Ge(100) surface via two different reactions: $[2 + 2]$ or $[4 + 2]$ cycloaddition between the π -conjugated aromatic ring and the Ge dimers, and the Lewis acid–base reaction in which the lone-pair electrons of pyridine are donated into the electron-deficient down-Ge atom in a Ge dimer. If adsorption occurs via cycloaddition, the surface dimers will be symmetric and the pyridine molecules will be located on top of the Ge dimers. If, on the other hand, adsorption occurs via a Lewis acid–base reaction, the Ge–N linkage formed by dative bonding is likely to keep the dimers buckled because the dangling bond of the electron-rich up-Ge atom maintains the buckled-up state after binding of the N atom of pyridine to the electron-deficient down-Ge atom. In addition, the pyridine molecules are expected to reside between the buckled dimer rows. The STM results presented in Figure 1 indicate that the adsorption of pyridine on Ge(100) proceeds preferentially via Ge–N dative bonding, similar to the case of alkylamines on Ge(100).⁸ We note that pyridine molecules bind to the down-Ge atoms of every second dimer on the same side of the dimer rows, forming the $c(4 \times 2)$ structure in order to minimize repulsive interactions between the adsorbed pyridine molecules. The intermolecular distance between the pyridine molecules in the $c(4 \times 2)$ structure would be comparable to the distance between pyridine molecules that are physisorbed on metal surfaces.⁹

In contrast to the case of pyridine on Si(100), the Ge–N dative bonding configuration on Ge(100) is found to be relatively stable. Most of the pyridine molecules ($\sim 90\%$) adsorbed on Ge(100) retain the single Ge–N adsorption configuration, even after a day under ultra-high vacuum ($p \approx 2 \times 10^{-10}$ Torr), and the rest of the pyridine molecules are found to desorb. The different behavior of adsorbed pyridine molecules on Si(100) and Ge(100) may be due to the difference in the barrier height of the transition state involved in the conversion of the adsorption state.

To investigate the detailed adsorption geometry of 0.25 ML of pyridine on Ge(100), we performed ab initio calculations within the local density approximation (LDA) using the Vienna ab initio simulation package (VASP). The simulated filled-state STM image generated from the optimized adsorption configuration (Figure 2a) is in good agreement with the experimental STM image (Figure 2b). The calculations show that (1) the Ge–N bond length (2.04 Å) is significantly longer than the covalent bond length (1.70 Å),⁸ indicating that the pyridine molecule datively binds to the down-Ge atom; (2) the Ge dimers are rearranged into a $c(4 \times 2)$ structure; (3) the adsorbed pyridine molecules retain their aromaticity; and (4) the plane of the aromatic ring is tilted to the surface (Figure 2c). More detailed theoretical results will be published elsewhere.

In summary, our results show that pyridine molecules adsorb on the electron-deficient down-Ge atoms of Ge(100) via Ge–N dative bonding to form perfectly ordered and oriented organic monolayers without loss of aromaticity. We anticipate that such well-defined ordered films of N-containing aromatic compounds will prove useful in the development of molecule-based devices and lithography.

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Supporting Information Available: Detailed experimental procedures and ab initio pseudopotential density functional calculations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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