Covalent Functionalization of Germanane

DISSERTATION

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Abstract

The group IV graphane analogues represent a new family of single atom-thick two-dimensional materials, in which the structure, stability and properties can be tailored for covalent ligand termination. These materials have attracted considerable interest as electronic, optoelectronic and topological materials. Here, we have established the synthesis, properties and surface functionalization of germananes. For the first time, we have reported gram-scale, millimeter-size hydrogen- and methyl-terminated germanane (GeH and GeCH₃), via the topotactic deintercalation of CaGe₂ with HCl and CH₃I, respectively. While the surface is oxidizing over time, the bulk of both GeH and GeCH₃ are resilient to air for several weeks. Compared with GeH’s band gap at ~1.6 eV, the band gap of GeCH₃ is increased by ~0.1 eV to 1.7 eV, producing a strong band edge photoluminescence with little layer dependence. Additionally, the thermal stability is improved from GeH at 75 °C to GeCH₃ at 250 °C. Furthermore, germanane samples with various ratios between methyl and hydrogen termination (Ge(CH₃)ₓH₁₋ₓ) were created from a co-deintercalation of CaGe₂ in the mixture of HCl and CH₃I solution. The structure and property of Ge(CH₃)ₓH₁₋ₓ changes pseudo-linearly with the x value, in a similar fashion as Vegard’s law. Finally, this alkylation method was successfully extended to various organohalides, producing a library of germanane terminated with different
organic ligands, which allows us to understand the influence of ligand size and electronegativity on electronic structure. Ligands that have a greater size and are more electronegative will expand the Ge-Ge bond length, thereby lowering the band gap. Simply by changing the identity of the organic ligand, the band gap of germanane can be tuned by ~15%, highlighting the power of surface chemistry to manipulate the properties of single-atom thick materials.
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Major Field: Chemistry
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Chapter 1: Introduction

Silicon and germanium, the workhorse materials of the semiconductor industry, are the most important and ubiquitous materials of the current era. Still, the neverending push toward device miniaturization calls for decreasing the size of electronic channels. The past decade has witnessed the creation of two-dimensional (2D), or single-atom-thick materials, which have led to the discovery of new phenomena and properties that are not present in the parent three-dimensional (3D) materials. Furthermore, the creation of single-atom thick derivatives of silicon and germanium oriented in a honeycomb arrangement are predicted to have direct band gaps compared to the indirect gap in the bulk of silicon and germanium, opening up light-emission based applications for these materials. Consequently, the creation of stable, robust single-atom thick 2D sheets of these semiconductor materials would have enormous implications in the electronics and optoelectronic industries.

The focus of this dissertation involves the synthesis, properties, and applications of functionalized germanium Graphane analogues. In this chapter, we first summarized the development of other 2D materials and their functionalization. Then we describe previous studies on the functionalization chemistry on Si/Ge (111) surfaces and the topotactic deintercalation chemistry that has been used to synthesize 2D silicon and germanium derivatives.
1.1 Two-Dimensional Materials

Historically, 2D materials are substances with a thickness of a few nanometers or less, where electrons and heat can transport freely in the 2D plane but restricted in the third direction. Here, by 2D materials, we specifically refer to materials in which the atomic organization and bond strength along two-dimensions are similar and much stronger than along a third dimension. In this section, we discuss 2D materials in three categories: 1) materials whose crystal structure features neural, single-atom-thick or polyhedral-thick layers of atoms with covalent or ionic bonding along two dimensions and van der Waals bonding along the third, and single-to few layers can be prepared via exfoliation; 2) materials that are synthesized from the chemical etching or deintercalation of a 3D ionic crystals like MXenes; 3) materials that can only be grown via the deposition of single-atom thick films on surfaces, such as group IV graphene analogues.

1.1.1 Materials from van der Waals Solids

The general physical approach to obtain a 2D material is through the exfoliation of layered van der Waals solids,\(^1\text{,}^6\) whose crystal structures are connected via strong covalent or ionic bonding within the 2D plane to form single-atom-thick or polyhedral-thick layers, whereas the layers are held together via van der Waals interaction in the third out of plane direction (Figure 1.1). Currently, the most well studied 2D materials are the single layers of graphite, hexagonal boron nitride (hBN), black phosphorus (BP) and layered transition metal dichalcogenides (LTMDs). Single layers of graphite (graphene) and hBN consist of single-atom-thick sheets of sp\(^2\)-hybridized carbon (or boron and nitrogen in hBN) in an extended honeycomb network (Figure 1.1a,b). While the single
layer BP, phosphorene, also consists of linked six-atom rings, those rings are puckered due to the sp³ hybridization of phosphorus atoms (Figure 1.1c). Additionally, phosphorene has two different edges, armchair and zigzag edges, featuring structural anisotropy. LTMDs refers to MX₂, where M = Ti, Zr, Hf, V, Nb, Ta, Re and X = S, Se, Te. The structure of LTMDs is comprised of hexagonally packed MX₆ octahedrons (for d⁰, d³, and some d¹ metals) or trigonal prisms (for d¹ and d² metals) share edges with their six nearest MX₆ neighbors within each layer to form 1T and 2H crystal structures, respectively (Figure 1.1d).
Figure 1. Crystal structure of layered van der Waals solids: (a) graphite, (b) hexagonal boron nitride, (c) black phosphorus [Reprinted with permission from ref 73. Copyright 2014 American Chemical Society.] and (d) layered transition metal dichalcogenides (MX₂, X = yellow spheres) with octahedral and trigonal prismatic coordination in 1T and 2H crystal structure, respectively [Reprinted with permission from ref 5. Copyright 2013 American Chemical Society.].

Though the exfoliation of LTMDs can be traced back to 1960s-1990s, when materials like MoS₂ and NbSe₂ were successfully exfoliated into single- or few-layers and characterized to some extent, the extensive research in 2D materials only started after the isolation of graphene in 2004. Part of the reason is that the techniques back in
1960s are limited and with the well-developed modern characterization methods, it is possible to locate, identify and characterize these extremely thin 2D materials nowadays.\cite{14,15} Optical microscopy and fluorescence quenching microscopy (FQM) are powerful techniques used to locate single and fewer layer flakes. To visualize 2D materials under optical microscopy, it is usually exfoliated or transferred onto a SiO$_2$/Si substrates with ideal dielectric (SiO$_2$) thickness.\cite{1,6} Here, the color of the dielectric-coated wafer depends on an interference effect from reflection off of the two surfaces of the dielectric. Single- and few-layer flakes on the surface of the dielectric modify the interference and create a color contrast between the flake and the substrate (Figure 1.2b).\cite{15} FQM uses an organic fluorophore whose fluorescence is quenched in the presence of single- or few-layer sheets via a fluorescence resonance energy transfer mechanism (Figure 1.2c).\cite{16} However, the above microscopy methods cannot conclusively tell if a flake is single, double or few layers. The most direct technique to determine the layer thickness is atomic force microscopy (AFM) (Figure 1.2a). Nevertheless, due to the difference between tip-substrate and tip-sample interaction, the sample height cannot be measured accurately in a single layer.\cite{17} This issue can be solved via the measurement of the folded edges or the steps in the exfoliated sample, where both interactions are between tip and sample.\cite{1,6}
Raman spectroscopy can be used to fingerprint the layer-thickness according to the change in peak position, width and intensity, allowing unambiguous and high-throughput identification of the number of layers, which is very useful in this emerging research area.\textsuperscript{18-22} Furthermore, systematically study in the Raman spectroscopy in the past decade has shown that besides determining the number of layers, it can also be used to determine the orientation of layers, the quality and types of edge, and the effects of perturbations, such as electric and magnetic fields, strain, doping, disorder and functional groups.\textsuperscript{23}

To further understand the structure and morphology of 2D materials, higher resolution microscopy is necessary. Transmission electron microscopy (TEM) and aberration-corrected scanning transmission electron microscopy (STEM) can provide detailed information on the crystallinity, layer sizes, interlayer interaction, stacking and
defects of these ultrathin flakes.\textsuperscript{24-33} Furthermore, since electronic states in graphene can be directly addressed by a metallic tip,\textsuperscript{34} scanning tunneling microscopy (STM) not only can measure the morphology and electronic structure of graphene,\textsuperscript{35, 36} but also can manipulate single atoms at specific points in order to build and characterize nanostructures.

In addition to the ultra-thin thickness, the intense interest in 2D materials is mainly due to the discovery of new and unique phenomena that is not present in their parent 3D materials. In single-layer graphene's band structure, the linear dispersion at the K point and massless Dirac fermions\textsuperscript{2} gives rise to novel properties like ambipolar field effect,\textsuperscript{1} high carrier mobility (\(\sim 200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\)),\textsuperscript{37, 38} leading to the detection of single molecule\textsuperscript{39} and the observation of room-temperature quantum Hall effect\textsuperscript{40, 41}, respectively. Studies have also shown that graphene has other unique properties like high thermal conductivity (\(\sim 5000 \text{ W/mK}\)),\textsuperscript{42} exceptional mechanicals strength,\textsuperscript{43} and even proton transport\textsuperscript{44}. Graphene-based materials have been proposed for a host of applications ranging from transparent electrodes for displays and solar cells\textsuperscript{45-48} to composite materials\textsuperscript{49}, barrister transistors,\textsuperscript{50} chemical sensors,\textsuperscript{51, 52} and high-speed and radio frequency logic devices\textsuperscript{53}.\textsuperscript{7}

LTMDs provide a large family of 2D materials, whose electronic properties can range from metals to semiconductors to insulators, exhibiting interesting phenomena like indirect to direct transition, excitonic effect, charge density waves and superconductivity.\textsuperscript{54} Some of the semiconducting LTMDs, for example, when \(M = \text{Mo}, \text{W}\), feature an indirect to direct band gap transition upon exfoliation into single layers.
Comparing the photoluminescence spectra of those single layers to double-, multi-layer flakes and bulk crystals, not only the intensity is several orders of magnitude stronger, the band gap emission energy also blue shifts (Figure 1.3c-e). This sizable direct band gap (1-2 eV) at single layer and recently reported nearly 100% photoluminescence quantum yield allows their applications in electronics and optoelectronics. Field-effect transistor (FET) devices built from monolayer MoS₂ have shown moderate carrier mobility (200 cm² V⁻¹ s⁻¹) and high on/off ratio (10⁸). Device application of LTMDs has also been established in photodetectors, solar cells, light-emitting diodes, lasing, and photocatalysts.
Figure 1. 3 Layer-dependent band structure, PL and absorption in MoS$_2$. (a,b) Calculated band structure of bulk (a) and monolayer (b) MoS$_2$. The solid arrows indicate the lowest energy transition. [Reprinted with permission from ref 4. Copyright 2010 American Chemical Society.] (c) PL of monolayer and bilayer MoS$_2$. Inset, layer-dependent quantum yield for 1-6 layers in log scale. (d) Absorption spectra (left axis) normalized by the layer number and the corresponding PL spectra (right axis) normalized by peak A. (e) Layer-dependent band gap energy of 1-6 layers of MoS$_2$. The band gap values were inferred from the energy of the indirect gap PL peak I and the direct gap PL peak A for 2-6 layers and monolayer, respectively. As a reference, the (indirect) band gap energy of bulk MoS$_2$ is shown as dashed line. [(c-e) Reprinted with permission from http://dx.doi.org/10.1103/PhysRevLett.105.136805, ref 3. Copyright 2010 by the American Physical Society.]
A single layer of hBN is known as “white graphene” due to its similar structure as graphene and its wide band gap\(^{67}\) (5.97 eV). Because of its atomically smooth surface,\(^{68}\) wide band gap and small lattice mismatch with graphite,\(^{69}\) hBN was found to be one of the best dielectric substrate for graphene to maximize graphene’s electronic performance.\(^{70}\) It has also been used as the dielectric layer in other 2D materials to protect fragile single layer materials due to its flatness, high air, thermal and chemical stability.\(^{71}\)

BP was reported to have high mobility and a small band gap (0.3 eV) back to 1960s.\(^{72}\) It was only recently that phosphorene was successfully exfoliated.\(^{73}\) Due to BP’s structural anisotropy, phosphorene’s electronic properties also differ in these two directions. The electron effective mass, for example, is several times lighter in the armchair direction than in the zigzag direction, and a strong angular-dependent transport was reported in few-layer BP.\(^{73, 74}\) Unlike semiconducting LTMDs, in which direct band gap is only observed in monolayers,\(^{3, 4}\) the bandgap of BP is expected to be direct for all thicknesses,\(^{73}\) a significant benefit for optoelectronic applications. The direct band gap is also layer-dependent, increasing from the bulk (0.3 eV) to single layer (1.5 eV),\(^{73}\) which are just the values between those of graphene and the semiconducting LTMDs. As a result, semiconductors with the band gap at nearly the entire range between 0 and 2 eV can now be provided with layered materials. Few-layer BP based FETs are reported to have an on/off ratios of \(~10^4-10^5\) and room temperature mobilities up to \(~200-1000\) cm\(^2\) V\(^{-1}\) s\(^{-1}\),\(^{73-75}\) making it a promising candidate for high-performance electronic and optoelectronic device applications. Compared with graphene and MoS\(_2\), phosphorene is
air sensitive, which will degrade under ambient condition in hours. This degradation can be suppressed by encapsulated with AlOₓ atomic overlayers or hBN or even by dipping in solvents like NMP to form a protecting layer over the surface.

1.1.2 MXenes

In the past five years, a new and large family of 2D materials, MXenes, was discovered. MXenes are produced by selective etching of the A element from the MAX (Mₙ⁺ₑAXₙ) phases (Figure 1.4), where “M” is an early transition metal (Ti, Nb, Mo, etc.), “A” is a main group IIIA or IVA element (Al, Si, Sn, etc.), “X” is carbon or/nitrogen, and n = 1-3. The MAX phases consists of [M₆X]ⁿ⁻ octahedrons that share edges with each other to form layered sheets, which are connected via M-A metallic bonding between the layers (Figure 1.4, top). The strong interlayer interaction makes it nearly impossible to get single- or few-layer thick materials via mechanical exfoliation. However, due to the fact that the bonding between M-X is much stronger than that between M-A, and A is a relative reactive species, the A layers can be selectively etched with aqueous HF at room temperature without disrupting the M–X bonds. This process is always aided with sonication to help delaminate the layers to obtain MXene phases, or MX layers that are terminated with –OH, –H, –O– and/or –F ligands. Currently, about nine MXenes have been produced by this method and other etchants like NH₄F and LiF with HCl were also reported. Scanning and transmission electron microscopy have been used to study the crystallinity and structure of MXenes.
Figure 1.4 Structure of MAX phases and the corresponding MXenes. [Reprinted with permission from ref 79. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.]

The high electronic conductivities\textsuperscript{83} and the hydrophilicity due the surface ligands indicates that MXenes would be promising candidates for many applications such as hydrogen storage media,\textsuperscript{85} catalysts support,\textsuperscript{86} conductive reinforcement additives, electrochemical energy storage like batteries\textsuperscript{87-89} and electrochemical capacitors.\textsuperscript{90, 91}

1.1.3 Germanene, Silicene and Stanene

As the counterpart of graphene for silicon, germanium and tin; silicene, germanene and stanene were predicted to be structurally stable and have novel and
fantastic physical properties akin to graphene such as linear energy dispersion near the K point, and nontrivial topological properties.\textsuperscript{92-94} While sharing similar properties with graphene, they have the advantage of being more easily integrated into the current semiconductor industry. Compared with graphene, the larger Si-Si/Ge-Ge/Sn-Sn interatomic distance weakens the $\pi$$\pi$ overlaps, resulting in a buckled structure with sp$^2$-sp$^3$ hybridization (Figure 1.5).\textsuperscript{95} The weak $\pi$$\pi$ bonding makes these materials incredibly reactive, and consequently they preferentially a fourth bond to stabilize the sp$^3$ hybridization.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{puckered.png}
\caption{Crystal structure of puckered silicene, germanene and stanene. (a) and (b) are side and top view, respectively. Atoms with different colors (red and yellow) are not in the same plane, but are of the same element. [Reprinted with permission from http://dx.doi.org/10.1103/PhysRevLett.107.076802, ref 94. Copyright 2011 by the American Physical Society.]}\end{figure}
However, silicon, germanium and $\beta$-tin, all preferentially crystallize into the diamond crystal structure type. Therefore, the synthesis of group IV graphene analogues can only be accomplished by deposition under ultrahigh vacuum conditions. It was demonstrated that silicene could be deposited on Ag (111) (Figure 1.6),$^{96}$ ZrB$_2$ (0001)$^{97}$ or Ir (111)$^{98}$ surfaces. Similar methods were used to grow germanene on Pt (111)$^{99}$ and Au (111)$^{100}$ surfaces; and stanene on Bi$_2$Te$_3$ (111)$^{101}$ surface. Unfortunately, all of them are grown on metal substrates, which will mask the 2D materials’ delicate electrical properties, making it impossible to check the theoretical predictions of strange quantum effects. Another problem of these 2D materials is their chemical instability.$^{102}$ Because these single layers can react with the air rapidly, the transfer of them into an insulating substrate or even direct measurement of electronic properties remains challenging. So far, there is only one experimental silicene device report,$^{103}$ where Al$_2$O$_3$ was used to encapsulate silicene together with the native Ag (111) substrate, and it was found that silicene has the Dirac-like ambipolar charge transport as predicted and a carrier mobility of 100 cm$^2$ V$^{-1}$ s$^{-1}$. 
Figure 1. 6 STM of silicene on Ag (111) surface. STM image of (a) clean Ag (111) surface, and (b) silicene on Ag (111). (c) Simulation of silicene on Ag (111) to describe the observed STM in (a) and (b). [Reprinted with permission from http://dx.doi.org/10.1103/PhysRevLett.108.155501, ref 96. Copyright 2012 by the American Physical Society.]

1.2 Covalent-Functionalization of 2D Materials

Since a 2D material is entirely made up of surface, its properties and reactivity are profoundly dependent on the substrate, its local electronic environment, and mechanical deformations. For example, simply by changing or modifying the supporting dielectric
substrate can dramatically change graphene’s carrier mobility and/or reactivity. The sensitivity to the environment is also why 2D materials can usually be used as sensors, though lacking selectivity. However, through chemical functionalization of 2D materials, we would not only develop a synthetic handle to tune the electronic structure of 2D materials via the identity of terminating substituent, but could also provide the approach to highly selective sensing application like the detection of biological agents.

Graphene and hBN are the two most chemical and thermal stable materials among all 2D materials. To functionalize them, relatively high energy is needed to break the sp$^2$ hybridization to form sp$^3$ hybridization. H$_2$ under a hot tungsten filament and F$_2$ at high temperature (600 °C) were used to terminate graphene with –H and –F, respectively. Though patterned hydrogen adsorption on graphene opens a band gap of around 450 meV near the Fermi level, half or full functionalization will disrupt the excellent carrier mobility in graphene, resulting in an insulator with a band gap of 3-5 eV. Graphene can also be functionalized with reactive intermediates like diazonium salts, benzyol peroxide, nitrenes, carbenes and arynes (Figure 1.7). Those chemical modification will open a band gap in graphene, change its carrier mobility and improve its solubility and processability. However, it is hard to control the percentage of functionalization due to the chemicals’ high reactivity and graphene’s region dependent reactivity. Similarly, hBN can be functionalized with nitrenes and hydroxyl.
LTMDs are consist of neutral layers and seem to lack the possibility for chemical functionalization if pristine. Nevertheless, chemical exfoliation can introduce sulfur vacancy into MoS$_2$ and the functionalization can be achieved on these vacancies by ligand conjugation of thiol.$^{119}$ Another route is to introduce negative charges on MoS$_2$ via chemical exfoliation and then use strong electrophiles like orangohalides or diazonium salts to quench the charge via covalent functionalization of organic ligands to sulfur.$^{120}$ However, both methods can only produce a low percentage of ligand coverage and it is also hard to control the coverage. The preparation of MXenens will always introduce covalently bound surface ligands to the transition metal (M) to offset the etching of main group element (A).$^{79}$ However, it is always a mixture of ligands and it is hard to control and quantify the percentage of each ligand, making it hard to study the ligand effect on the properties on MXenens.
Hydrogen-terminated silicene (SiH) is predicted to have an indirect gap at 2.9 eV, while termination with different ligands converts it into a material with a direct gap between 2.1 to 2.5 eV (Figure 1.8).\textsuperscript{5} In heavier elements, novel physical properties like topological insulators have been predicted when germanium or tin is functionalized with specific ligands (Figure 1.9),\textsuperscript{121,122} opening the door for novel lateral heterostructures between topological and conventional states. Experimentally, no direct covalent functionalization has been reported in silicene, germanene or stanene. However, functionalized silicene derivatives have been reported\textsuperscript{123} and will be summarized in the last section of this chapter and functionalized germanene derivatives will be covered in details in this dissertation.
Figure 1. 8 Calculated band structure in functionalized silicene. Silicene was functionalized with (a) H, (b) half H and half hydroxyl (OH), (c) methyl CH₃, and (d) acetylene C≡CH, respectively. [Reprinted with permission from ref 5. Copyright 2013 American Chemical Society.]
1.3 Functionalization on Si/Ge (111) Surface

Though there is no experimental study on the direct functionalization of silicene or germanene, the functionalization chemistry on Si/Ge (111) surfaces has been well established (Figure 1.10), where they can be passivated with hydrogen or organic ligands to improve the stability. Upon exposure to air, the surface of Si/Ge (111) substrates will oxidize immediately. Fortunately, after treating with degassed 40% aqueous NH$_4$F or aqueous HF for several minutes, surface oxides will be removed and flat hydrogen terminated Si (111) and more rough hydrogen-terminated Ge(111) surfaces can be achieved, respectively. Subsequently, halogenation on Si (111) can be achieved via
radical reaction by treating H-Si (111) with halogen sources like PCl₅, Cl₂, CCl₃Br or N-bromosuccinimide, under high temperature (80-100 °C) with benzoyl peroxide as initiator or under UV light.¹²⁹-¹³¹ Besides the fact that these similar halogenation methods can be applied to Ge (111),¹³², ¹³³ atomic flat Cl-Ge (111) can also be obtained through a mild approach by treating the oxidized Ge (111) wafer with 10% aqueous HCl for 10 mins.¹³⁴

There are various approaches to attaching organic ligands to Si/Ge (111) surfaces, depending on the starting precursors (Figure 1.10). Hydrosilylation or hydrogermylation is the reaction between H-Si/Ge (111) and alkene or alkyne under conditions like high temperature (>150 °C), UV light or the addition of radical initiator or catalysts. During these reactions, the unsaturated bond is inserted into Si/Ge-H bond, producing alkyl and alkenyl terminated Si/Ge (111).¹³⁵-¹³⁹ Direct reaction between H-Si (111) and Grignard reagent is also reported while the same chemistry is not working for H-Ge (111).¹³⁸ Another approach is to react halogen-terminated Si/Ge (111) with strong organic base like Grignard reagent or organolithium.¹²⁹, ¹⁴⁰, ¹⁴¹ While hydrosilylation/hydrogermylation is a quick reaction that can be completed within a couple of hours, halogenation/alkylation can allow the attachment of small ligands like methyl or acetylene which would give higher surface coverage compared with bulky ligands.¹³², ¹⁴², ¹⁴³ Furthermore, thiols can also be covalently grafted to Ge (111) surface through the reaction between H-Ge (111) and thiols.¹⁴⁴
While H-Si (111) and Br-Si (111) surfaces are stable in air for several minutes, H-Ge (111) surface will oxidize immediately upon exposure to air while Cl-Ge (111) surface are reported to oxidize after an hour of air exposure. Though not air-stable over long periods, these hydrogen- or halogen-terminated surfaces indeed serve as useful precursors for the organic functionalization reactions. The organic ligand terminated Si/Ge (111) surfaces are remarkably air stable with alkyl-S-Ge (111) stable for up to 12 hours and alkyl-Si/Ge (111) stable from several days to weeks in air or from 30 minutes to several hours in boiling water or organic solvents. The organic
functionalized surfaces are also thermally stable to some extent with C-Ge/Si bonds more thermally stable than S-Ge bond. Alkyl-S-Ge (111) is stable up to 177 °C and complete desorption is found when heated to 277 °C. While alkyl-Ge (111) surface is thermally stable up to 200-400 °C, alkyl-Si (111) is stable at 300-350 °C. From all the alkyl-Ge (111) reactions, only halogenation/alkylation and neat thermal hydrogermylation yield well-ordered monolayer surface and enhanced stability.

1.4 Zintl Phase and Deintercalation Chemistry

The synthesis of one-dimensional inorganic polymers and single rings of polysilanes, polygermanes, and polystannanes from small molecules has been well developed from the reaction between X-(R2M)2-X and alkali metals or between X-(R2M)2-X and R3MLi, where X refers to halogens, R refers to organic ligands and M refers to Si/Ge/Sn. To date, there have been no synthetic routes for preparing group IV graphane analogues from small molecule precursors due to the lack of a mechanism for controlling growth in two dimensions.

However, the layered Zintl phases, CaSi2, CaGe2, and BaSn2, are comprised of puckered honeycomb [Si]+n, [Ge]+n, and [Sn]+n graphane-like layers, held together by the group II [M2+] cations (Figure 1.11, left). Consequently, the preparation of germanium graphane analogues relies on developing soft chemical processes that can topotactically deintercalate the M2+ cations while maintaining the structure and covalently terminating the anionic group IV layers (Figure 1.11). Furthermore, those puckered honeycomb frameworks are structurally analogous to the Si/Ge (111) surfaces. In principle, the established surface functionalization chemistry on Si/Ge (111) surfaces...
can be used to modify the ligand if the topotactic deintercalation can produce either hydrogen- or halogen-terminated frameworks.

**Figure 1. 11 Scheme of topotactic deintercalation.** Blue: group IVA elements, yellow: alkali metals, red: functional ligands.

The topotactic deintercalation of CaSi$_2$ using HCl can be traced back to Wöhler in the 1860s and Kautsky in the 1920s, and the structure and properties were partially resolved in the 1980s and 1990s.$^{152-159}$ It was reported that siloxane (Si$_6$H$_3$(OH)$_3$) preferentially forms at temperatures greater than 0 °C and layered polysilane (Si$_6$H$_{6-x}$(OH)$_{1-x}$ (x < 1)) forms at -30 °C.$^{152,153,157}$ These structures are silicon graphane analogues, or silicanes, with –H and –OH or mostly –H terminal substituents, respectively. Compared with the indirect band gap of crystalline silicon (1.1 eV), siloxene has a direct band gap at around 2.4 eV with strong photoluminescence (PL).$^{153}$ Using these layered polysilane (Si$_6$H$_{6-x}$(OH)$_{1-x}$ (x < 1)) as precursors, the same surface
functionalization chemistry developed on Si/Ge (111) surfaces applied to synthesize organic ligand terminated silicanes,\textsuperscript{160-162} or silicon graphane analogues, in the past decade with approaches like halogenation/alkylation, hydrosilylation, and even direct reaction between Grignard reagents and Si$_6$H$_6-x$(OH)$_{1-x}$, featuring PL ranging from 2.7 to 2.9 eV.

However, the topotactic deintercalation of CaSi$_2$ in aqueous HCl readily produces partially OH-terminated SiH$_x$(OH)$_{1-x}$ due to the significantly stronger Si–O bond (800 kJ/mol) compared with the Si–H bond (300 kJ/mol)\textsuperscript{163}. This ambiguity in surface functionalization convolutes efforts to correlate the effects of surface functionalization on the optoelectronic properties of these single-atom thick semiconductors. In contrast, the difference of bond strength is much smaller between Ge–O (660 kJ/mol) and Ge–H (320 kJ/mol)\textsuperscript{163} and furthermore, any native germanium oxide or hydroxide termination is readily dissolved in aqueous HCl, thereby producing pure germanane (GeH). Indeed it was reported by Brandt and Stutzmann that CaGe$_2$ thin films grown on germanium wafers can be topotactically deintercalated to form GeH, with little surface oxidation.\textsuperscript{164} There are no reports on the further functionalization of hydrogen terminated germanane (GeH). We attempted to apply functionalization chemistry developed from Si/Ge (111) surfaces to GeH and found that although halogens like bromine could be grafted to form Ge-Br bond, the radical reaction will amorphize the germanium framework. Furthermore, as will be discussed in the next chapter, GeH will thermally amorphize at temperatures higher than 75 °C and makes reactions that require high temperature not applicable. Thus, new routes toward functionalization of germanane need to be developed.
In this dissertation, we highlight the synthesis and stability study of both the hydrogen- and methyl-terminated germanium graphane analogues. We also show that the methylation chemistry can be extended to various organic functional groups. Finally, the influence of the identity of surface-terminating ligand and the percentage of organic functionalization on the electronic structure of these 2D materials are established.

1.5 References for Chapter I


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Chapter 2: Hydrogen-Terminated Germanane (GeH)

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2.1 Introduction

There has been considerable excitement about the use of two-dimensional (2D) van der Waals materials in optoelectronic applications such as photodetectors and solar cells, due to the change in their electronic structure when exfoliated into single layers.1-8 Similarly, significant changes in electronic structure are expected when three-dimensional semiconductors such as Si and Ge are converted into their 2D analogues.9-11 Layered silicon and germanium solids have been synthesized from the topotactic deintercalation of layered Zintl phases such as CaSi$_2$ and CaGe$_2$.12-14 While numerous studies have shown that the silicon lattice oxidizes immediately in air,12, 15 there is only one report on GeH thin films grown on Ge (111) substrate and the air and thermal stability is not rigorously characterized,13 which is an essential prerequisite for any application. Furthermore, compared with the previous thin film GeH, the preparation of
bulk, multilayered crystals greatly facilitates the characterization of elemental composition, structure, and properties using conventional solid-state methods.

Herein, we have synthesized for the first time, millimeter-scale crystals of a hydrogen-terminated germanium multilayered graphane analogue (germanane, GeH) from the topotactic deintercalation of CaGe$_2$. GeH has a layered structure and features a band gap of 1.59 eV. The surface layer of GeH only slowly oxidizes in air over the span of 5 months, while the underlying layers are resilient to oxidation. The GeH is thermally stable up to 75 °C; however, above this temperature amorphization and dehydrogenation begin to occur. Additionally, by preparing GeH via the deintercalation with different acids, we confirmed that the low temperature amorphization is intrinsic to the GeH structure. Finally, we performed high-level theory calculations of the electronic structure, predicting a direct band gap of 1.53 eV and an electron mobility five times higher than that of bulk Ge.

2.2 Experimental

2.2.1 Materials

Germanium powders and calcium turnings were obtained from ACROS Organics and used without any further purification. Aqueous HCl and acetic acid were obtained from Fisher Scientific and used without any further purification. Methanol, aqueous HBr and HI were obtained from Sigma-Aldrich and used without further purification. All water used here was purified with Milli-Q Reference from Millipore.
2.2.2 Sample Synthesis and Preparation

To synthesize calcium germanide (CaGe$_2$), calcium turnings were cut into small pieces right before the reaction. Around 1g of germanium and 290 mg of calcium, with the stoichiometric of 1:1.05, were loaded into a feet long quartz tube inside a glovebox. The tube was then connected to a Schlenk line, evacuated and sealed under vacuum. In a tube furnace, the sealed quartz tube was heated up to 950 °C at the ramping rate of 10 °C/min and stayed at 950 °C for 18 hrs, followed by slowly cooling down to 400 °C at the rate of 5 °C/hr and then to room temperature at the rate of 40 °C/hr.

To get GeH flakes, CaGe$_2$ crystals were put in an extraction thimble, fully immersed in concentrated aqueous HCl in a beaker, with a stir bar at the bottom of the thimble. The reaction was running at -40 °C for around a week. For purification, GeH flakes were washed with MilliQ-water followed by methanol, and then dried on a Schlenk line.

To study the thermal stability and amorphization of GeH, different versions of GeH were made by replacing the proton source, concentrated aqueous HCl, with concentrated aqueous HBr, HI, acetic acid and dilute HCl. The reaction temperature ranged from -40 °C to room temperature while the reaction time varies from 5 to 14 days (Table 2.1).
Acid (Kα) | Temperature (°C) | Time (days)  
---|---|---  
Conc. HCl (10⁶) | -40 | 8  
Conc. HBr (10⁹) | -10 | 6  
Conc. HI (10¹⁰) | -40 | 11  
Conc. HCl (10⁶) | 25 | 5  
Acetic acid (1.7 x 10⁻⁵) | 25 | 14  
1.6 M HCl (10⁶) | 25 | 10  

Table 2.1 Synthesis conditions for different GeH.

For thermal stability study, GeH flakes were annealed every 25 °C from 75 to 200 °C for 4 hours, respectively, under the flowing of 5% H₂ in Ar, and then cooled down to room temperature for characterizations. This process is repeated for all the GeH samples prepared with various acid.

2.2.3 Instrumentation

X-ray diffraction (XRD) was measured using Bruker D8 powder X-ray diffractometer. The room temperature XRD patterns of CaGe₂ and GeH were collected under capillary mode, while the temperature-dependent XRD patterns were collected under flat plate mode. Fourier transform infrared spectroscopy (FTIR) were collected on a Perkin-Elmer Frontier Dual-Range FIR/MidIR spectrometer that was loaded in an Ar-filled glovebox. The Raman spectra were collected using 633 nm (He-Ne red laser) illumination on a Renishaw InVia Raman equipped with a CCD detector. X-ray photoelectron spectroscopy (XPS) was collected using a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a monochromated (Al) X-ray gun. The Ar ion was used to etch the top layer of GeH, and the etch rate was calibrated using SiO₂. Transmission electron microscopy (TEM) was collected on CM200 from Philips. Diffuse reflectance absorption (DRA) was collected using a PerkinElmer Lambda 950 UV/Vis
spectrometer, with a diffuse reflectance integrating sphere attachment. X-ray fluorescence (XRF) measurements were performed using an Olympus DELTA hand-held X-ray fluorescence analyzer. Thermogravimetric analysis (TGA) was performed using a Q-500 thermogravimetric analyzer. Samples were analyzed from room temperature to 375 °C at a ramping rate of 10 °C/min under the flowing of N₂ at the rate of 50 ml/min.

The pair distribution function (PDF) measurements were performed at the 11-ID-B beamline at the Advanced Photon Source at Argonne National Laboratory using high-energy X-ray radiation (58–60 keV). For the sample preparation, the GeH flakes were finely ground and loaded into a kapton capillary tube, which was sealed with epoxy at both ends. During the measurement, a 2D image plate camera was used with a sample to detector distance of 188.248 mm, as calibrated by using a CeO₂ standard and Fit 2D software. The scattering from the kapton tube was measured independently and subtracted as a background. Fit 2D software was used to integrate the raw data to get S(Q). The real space PDF, or G(r), was obtained using PDFgetX3 software. The PDFgui program was used to refine the crystal structures. For temperature-dependent PDF, variable temperature data was collected by ramping the temperature from room temperature to 250 °C at a rate of 0.5 °C/ min. Each data set was collected over a time span of 3 minutes and a temperature range of 1.5 °C.

2.3 Results and Discussion

2.3.1 Structural Characterization

After annealing at 950 °C, highly crystalized CaGe₂ was formed in the β-phase, confirmed with XRD (Figure 2.1b, d). This β-CaGe₂ has six germanium layers per unit
cell (R-3m) with the lattice parameter of $a = 3.987 \, \text{Å}$, $c = 30.0582 \, \text{Å}$ ($c/6 = 5.097 \, \text{Å}$). After reacting with HCl, the big CaGe$_2$ crystal trunks were automatically exfoliated into flakes, yielding crystallites of GeH that are 2-3 mm in diameter and <100 μm in thickness (Figure 2.1c). XRD pattern (Figure 2.1e) of GeH confirms that it can be fit to a 2H unit cell (2 GeH layers per hexagonal c-unit cell spacing) with $a = 3.88 \, \text{Å}$ and $c = 11.0 \, \text{Å}$ (5.5 Å per layer). However, with recent synchrotron diffraction data, we found that a 6R unit cell (6 GeH layers per hexagonal c-unit cell spacing) with $a = 3.97 \, \text{Å}$ and $c = 33.1 \, \text{Å}$ (5.5 Å per layer) gives out better refinement results with the diffraction pattern. Compared to the original CaGe$_2$, the hydrogen-terminated germanane is slightly contracted in the $a$-direction but expanded in the $c$-direction due to the replacement of Ca$^{2+}$ with two Ge-H bonds between each layer. These lattice parameters do not correspond to any of the previously reported allotropes of germanium.$^{20, 21}$ The narrower full-width-half-maximum (FWHM) of the (100) (or (012) in 6R) and (110) diffraction reflections ($\sim 0.4^\circ$ in 2$\theta$) compared to the (002), (011), and (112) (or (006), (104) and (116) in 6R) peaks ($\sim 1.3^\circ$ in 2$\theta$) indicates that there is a significant amount of disorder along the c-axis, which is common in layered materials. This interlayer disorder and the lack of more peaks precludes Rietveld structural refinement with the in-house XRD pattern.
Figure 2. 1 Topotactic synthesis of GeH. (a) Scheme of topotactic deintercalation of CaGe$_2$ into GeH. (b,c) Optical images and (d,e) XRD of CaGe$_2$ (b,d) and GeH (c,e) crystals with select crystals on graph paper with a 1mm grid.
In contrast to XRD, which measures the averaged long range structure, PDF treats Bragg and diffuse scattering on an equal basis, and is used to unravel the short and medium range atomic arrangement in various materials from amorphous to crystalline.\textsuperscript{22-27} Thus, it is a really powerful method to solve the structure of materials with varying degrees of disorder, like the GeH here. In the measurements, the PDF gives us the probability of finding an atom at a given distance $r$ from another atom. In other words, it measures the atom-atom distance distribution.

The PDFs of crystalline Ge and GeH at room temperature directly confirms the honeycomb 2D network of germanium atoms in GeH. The structural models of GeH and crystalline Ge are shown in Figure 2.2 a and b, respectively. They both consist of hexagonal, puckered sp$^3$ layers of germanium atoms with similar Ge–Ge bond lengths and Ge–Ge–Ge bond angles (Figure 2.2c and highlighted in red boxes in Figure 2.2a,b). Compared with the G(r) of crystalline Ge, GeH has systematic absent interactions at 5.66, 7.35, and 8.95 Å (Figure 2.2d) that arise in 3D crystalline Ge. In Ge, these peaks correspond to Ge-Ge pairs between atoms in different (111) layers (Figure 2.2b, arrows). All other peaks can be indexed to the Ge-Ge pairs within a single Ge (111) plane (Figure 2.2c). The distance of the Ge atoms on a particular colored ring from the central Ge atom in Figure 2.2c corresponds to the same color peak in the PDF of Figure 2.2d. The large interlayer disorder of GeH prevents the observation of scattering between any interlayer Ge–Ge pairs.
**Figure 2. 2 PDF of Ge and GeH.** Structural models of germanane (a) and crystalline germanium (b), both of which have a hexagonal, sp$^3$-puckered layer of germanium atoms ((c), boxes in (a) and (b)). (c) A single (111) plane of crystalline germanium, representing a single layer of GeH. The distance of the germanium atoms on a certain colored ring from the central germanium atom corresponds to the same color peak in (d). (d) PDFs of GeH and Ge, data are truncated at 10 Å to highlight the differences. The starred peaks correspond to the Ge–Ge pairs arrowed in (b).
This obtained room temperature PDF data was refined to elucidate the structure of GeH (Figure 2.3). Since the sample that analyzed in the PDF had trace amounts of crystalline Ge, the data was refined with two different phases. The first phase was nanocrystalline GeH with a 2H P6₃mc space group, anisotropic thermal factors and a refined spherical envelope function. Since the only difference between 2H and 6R unit cell is the stacking order and as mentioned above, only in plane Ge-Ge pairs were observed in the PDF of GeH, there should be no difference in using P6₃mc or R-3m space group for the first phase. The second phase was crystalline Ge with an Fd-3m space group, isotropic thermal factors, and no spherical envelope function. The refinement that incorporates both phases can accurately account for all observed peaks, and produce a decent fit from 1-30 Å with an Rw value of 0.16 (Figure 2.3 and Table 2.2). The percentage of crystalline Ge impurity was refined to ~5%. In GeH, a large out-of-plane thermal factor (U₃₃) of around 0.6 Å² was observed for the Ge atoms, compared to the in-plane thermal factors (U₁₁ = U₂₂) of 0.02 Å², reflecting a large distribution of interlayer thicknesses. Other models of the 2D germanane framework such as a Cmca framework that resembles the hydrogenated orthorhombic black phosphorus structure,²⁸ or the previous reported Ge allotropes²⁰, ²¹ do not give reasonable fits to the room temperature PDF data. However, we would like to point out that the large interlayer thermal factor (U₃₃) possibly indicates that a larger box model containing multiple Ge layers may more accurately model the distribution of the interlayer spacing and give us a more reasonable thermal factor.
Figure 2. 3 Refined PDF results of GeH. The blue and red curves are the experimental and calculated data, respectively, while the green curve is the difference between them. Inset is a model of GeH structure with the calculated bond length and bond angle.

<table>
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<tr>
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<td>Fd-3m</td>
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<tr>
<td>$a$ (Å)</td>
<td>3.986(9)</td>
<td>5.648(8)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>11.03(36)</td>
<td></td>
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<tr>
<td>Atomic position of Ge(1)</td>
<td>0, 0, 0.0177(31)</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>Atomic position of Ge(2)</td>
<td>2/3, 1/3, 0.09</td>
<td></td>
</tr>
<tr>
<td>Ge(1) $U_{11} = U_{22}$ (Å$^2$)</td>
<td>0.02(6)</td>
<td>0.0062(36)</td>
</tr>
<tr>
<td>Ge(1) $U_{33}$ (Å$^2$)</td>
<td>0.62(38)</td>
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<tr>
<td>Ge(2) $U_{11} = U_{22}$ (Å$^2$)</td>
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<td>Ge(2) $U_{33}$ (Å$^2$)</td>
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</tr>
<tr>
<td>$R_w$</td>
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Table 2. 2 Two-phase refined result of GeH.
To further confirm hydrogen termination, we performed FTIR, Raman spectroscopy and XPS on the germanane product. Transmission mode FTIR (Figure 2.4) of samples ground up and pressed into KBr pellets shows extremely strong Ge-H stretching at ~2000 cm\(^{-1}\) and multiple wagging modes at 570, 507, and 475 cm\(^{-1}\). Additionally, weak vibrational modes at 770 and 825 cm\(^{-1}\) are also observed. These two vibrations also occur in the spectra of amorphous Ge\(_{0.7}\):H\(_{0.3}\) thin films and have been assigned by M. Cardona et al. to originate from bond-bending Ge-H\(_2\) modes from nearest neighbor Ge atoms.\(^{29,30}\) Thus, we hypothesize that these vibrations correspond to Ge-H\(_2\) bond-bending modes from neighboring Ge atoms at the edges of each crystalline germanane sheet and/or to Ge-H\(_2\) bonds within the lattice arising from Ge vacancies. We do not observe the presence of the broad, intense Ge-O-Ge and Ge-O vibrational modes that occur between 800 and 1000 cm\(^{-1}\).\(^{31}\)

![Figure 2. 4 FTIR of GeH.](image)
From Raman spectroscopy (Figure 2.5), the main Ge-Ge stretch in GeH occurs at 302 cm⁻¹, which is slightly blue-shifted compared to the 297 cm⁻¹ E₂ Raman mode for crystalline germanium. In addition, a second vibrational mode emerges at 228 cm⁻¹. We performed ab initio calculations of the Γ-point phonon modes in GeH using Perdew-Burke-Ernzerhof (PBE) functionals as implemented in VASP.³², ³³ These calculations predict the presence of Ge-based A₁ and E₂ Raman modes (assuming a C₆v point group) that occur at 223 and 289 cm⁻¹, respectively, which are in good agreement with the observed Raman modes. The symmetries of the vibrational modes are shown in the inset of Figure 2.5.

**Figure 2.5 Raman of GeH (blue) and Ge (red).** The middle inset highlights the difference in energy of the E₂ peak between GeH and Ge while the right insets are schematic illustrations of the A₁ and E₂ vibrational modes.
XPS measurements are also indicative of a single germanium oxidation state. XPS analysis of the Ge 2p$_{3/2}$ peak for GeH shows a single peak at 1217.8 eV, which is indicative of Ge$^+$. A shift in the Ge 2p$_{3/2}$ peak energy from Ge$^0$ (1217.0 eV) is expected since hydrogen is more electronegative than germanium (Figure 2.6). A control Ge (111) wafer with surface oxide shows a mixture of germanium oxidation states ranging from Ge$^+$ (1217.0 eV) to Ge$^{2+}$ (1218.9 eV) to Ge$^{4+}$ (1221.4 eV).

![Figure 2.6 XPS of Ge 2p in GeD (blue) and Ge (111) wafer.](image)

TEM analysis indicates the product has a layered morphology with individual layers having less contrast than the 10 nm lacey carbon support grid (Figure 2.7a,b). The energy dispersive X-ray spectrum has a strong Ge signal, an absence of Ca and O signals, and the presence of trace amounts of Cl. The Cl:Ge ratio was estimated to be 2:98 (Figure 54).
Figure 2.7c is an electron diffraction pattern taken orthogonal to the layers, showing a hexagonal arrangement of diffraction peaks that occur in the $a$- and $b$-directions. These data further confirm that the crystallinity of the germanium layered framework is preserved upon HCl treatment, and there is a strong registration in the stacking between each layer. The GeH electron diffraction pattern can be indexed to a simple hexagonal unit cell with $a = b \approx 3.87$ Å, assuming a [001] zone axis.
Figure 2. 7 TEM of GeH. (a) Low-magnification and (b) magnified TEM micrograph of GeH platelets. (c) Electron diffraction pattern of platelets collected down the 0001 zone axis. (d) Energy dispersive X-ray spectroscopy of the GeH sheets.

2.3.2 Optical Properties and Band Structure

The optical properties of germanane were investigated by DRA. This silver-black material has a broad absorption over visible wavelengths, and a linear approximation of the absorption edge suggests a band gap of approximately 1.59 eV (Figure 2.8a). The Tauc/Davis-Mott expression for materials with 2D densities of states predicts that the
absorbance $A(\hbar \omega)$ at photon energy $\hbar \omega$ near the band edge would be a step function with a discontinuity in absorbance at the band gap if the band gap was direct allowed. If the band gap was indirect allowed, the absorbance would be proportional to $\hbar \omega - E_g' \pm E_p$, where $E_g'$ is the indirect gap and $E_p$ is the energy of a particular phonon mode. However, it has been experimentally established that the Tauc/Davis-Mott approximations of absorption cannot unambiguously determine the transition mechanism for fundamental absorption for bulk materials with 2D densities of states.\textsuperscript{34-36} We modeled the absorbance assuming direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden gaps using both 2D and 3D densities of states (Figure 2.9). All of these plots estimated fundamental gaps ranging from 1.48 to 1.60 eV. These analyses are complicated by a broad Urbach edge at the lower end of the absorption tail, which is often indicative of a large doping concentration or disorder. The presence of photoluminescence is often a stronger test of a direct band gap. Previously reported studies of GeH thin films proposed that GeH is a direct band gap material with a fundamental absorption gap at 1.8 eV based on photothermal deflection spectroscopy and photoluminescence that occurs at 0.45 eV lower, or 1.35 eV.\textsuperscript{37} We did not observe any photoluminescence from 1.1 to 1.8 eV when exciting from 1.38 to 1.96 eV at temperatures ranging from 14 to 300 K. This lack of photoluminescence and linear slope in our samples might suggest that germanane has an indirect band gap. However, the lack of photoluminescence alone is not sufficient evidence of an indirect gap. A direct band gap material could lack photoluminescence if there is a large concentration of nonradiative defect states or impurities in the sample or if the material possesses unique surface or edge states. The presence of any of these can
quench photoluminescence and also contribute to the observed bowed Urbach edge. Therefore, further optimization of the growth and etching chemistry will be necessary before dismissing the potential existence of a direct band gap. Also, we propose that more direct measurements, such as angle-resolved photoemission spectroscopy, as well as additional temperature-dependent absorption studies are necessary to completely conclude whether germanane has a direct or indirect band gap, especially since our theory predicts GeH to have a direct band gap.

**Figure 2. 8 DRA and band structure of GeH.** (a) DRA spectrum of GeH plotted as $h\nu \alpha$ vs photon energy highlighting a 1.59 eV band gap. (b) Electronic band structure of an isolated single layer of GeH calculated using HSE-06 theory including spin-orbit coupling predicting a 1.56 eV direct band gap. The hole and electron effective masses for each extrema are indicated in red.
Figure 2. 9 Absorption spectrum of GeH fitted to different band structures. The fitting is according to Tauc/Davis-Mott expressions of 2D densities of states and 3D densities of states and a 37.5 phonon vibration (deduced via the 300 cm\(^{-1}\) Raman shift) was determined.
Band structure calculations suggest that germanane is a direct band gap material both as isolated layers and in the crystal structure having two layers per unit cell. We used the density functional theory (DFT) code VASP\textsuperscript{32, 33} to optimize the geometry and calculate the band structure of isolated single layer and two-layer unit cell GeH. The interactions between cores and electrons were described for relaxation by projector augmented wave (PAW) pseudopotentials\textsuperscript{38} within the PBE exchange-correlation function\textsuperscript{39, 40} with a plane-wave cutoff energy of 600 eV. van der Waals interactions between the layers were included using the DFT-D2 method by Grimme.\textsuperscript{41} For the two-layer structure, the unit cell was modeled as a P6\textsubscript{3}mc unit cell with relaxed lattice parameters of $a = 4.05$ Å and $c = 10.56$ Å, thus having a 5.3 Å layer spacing. For the isolated single-layer structure, the calculations were performed in a unit cell with 20 Å of additional vacuum between GeH layers. To obtain an accurate description of the band gap in this system, the hybrid HSE06\textsuperscript{42-44} exchange-correlation function was used. With this function we obtain a direct gap at the $\Gamma$ point of 1.56 eV for an isolated layer (Figure 2.8b) and 1.53 eV for the two layer unit cell, which is in excellent agreement with the observed experimental band gap. The calculated band gap for the two-layer unit cell at the A point of the Brillouin zone is $\sim$1.77 eV. The difference in energy between the conduction band minimum at the M point and the valence band maximum at $\Gamma$ is 2.48 and 2.33 eV for an isolated layer and two-layer unit cell, respectively. In both cases, spin-orbit splitting at the $\Gamma$ valence band maximum is 0.2 eV.

Additionally, the effective masses of the conduction and valence bands at each extremum were calculated for the isolated single layer and are shown in Figure 2.8b. In
bulk crystalline germanium, the conduction band minima occur in the four equivalent valleys at the L <111> point, which have much higher effective mass ($m_{\text{elL}}^* = 1.64$) than the conduction band valleys at $\Gamma$ ($m_{\text{el}\Gamma}^* = 0.041$). However, since GeH can be thought of as hydrogen-terminated isolated (111) sheets of germanium, we are effectively eliminating the L wavevector in the Brillouin zone. We also calculated from first principles the phonon-limited electronic mobility for an isolated single layer, obtaining a high mobility of 18,195 cm$^2$ V$^{-1}$ s$^{-1}$. This five times increase in electron mobility from bulk Ge (3,900 cm$^2$ V$^{-1}$ s$^{-1}$) is consistent with the reduced electron effective mass in GeH.

2.3.3 Air Stability

The potential utility of germanane for any optoelectronic or sensing device strongly hinges on its air and temperature stability. Some previous reports state that hydrogen-terminated Ge (111) surfaces having the same atomic configuration as GeH are resistant to oxidation when the Ge surface has minimal defects, although some debate remains. Because FTIR spectroscopy is a sensitive probe of the presence of Ge-O vibrational modes at 800-1000 cm$^{-1}$, we exposed the GeH samples in air for a series of times and the FTIR was measured under the attenuated total reflectance (ATR) mode. Virtually no change from 800 cm$^{-1}$ to 1000 cm$^{-1}$ was observed after 60 days’ air exposure, thus proving that the bulk of GeH resists oxidation (Figure 2.10a). Additionally, time-dependent XPS was performed to probe changes in the Ge oxidation state of the surface after exposing these layered GeH crystals to air (Figure 2.10b), and the percentage of each germanium oxidation state for all spectra was calculated by applying a standard Gaussian fit. After 1 month of exposure to air, a Ge$^{2+/3+}$ shoulder emerges at $\sim$1219.3 eV
(19.5% Ge²⁺³⁺). This peak becomes more intense after 5 months of air exposure (29.7% Ge²⁺³⁺). After Ar etching the top 0.5 nm (<1 layer), the Ge²⁺³⁺ almost completely disappears with 10.1% Ge²⁺³⁺ remaining. Together, the XPS and FTIR suggest that only the surface of GeH becomes oxidized over time, while the bulk is resilient to oxidization.

**Figure 2.10 Air stability of GeH.** (a) Time-dependent FTIR of a GeH flake after exposure to ambient atmosphere for up to 60 days, collected via reflection mode, highlighting minimal changes in the relative intensity of the Ge-H to Ge-O vibrations. (b) Time-dependent Ge 2p XPS spectra of germanane immediately after exposure to atmosphere, after 1 day, 1 month, 5 month and after 5 months, followed by Ar etching by 0.5 nm.

### 2.3.4 Thermal Stability

The temperature stability of germanane was probed via various methods like TGA, DRA, XRD, and Raman. It is shown that DRA is the most sensitive method to detect any thermal amorphization. TGA shows a ~1.1% mass loss at 200-250 °C, which
is close to the expected mass loss of 1 equivalent of hydrogen in GeH, as well as a 1.7% mass loss of that occurs between 320 and 355 °C (Figure 2.11a). This second mass loss likely corresponds to the loss of Cl (3.6% molar). ATR-FTIR measurement in the far IR range indicates that partial germanium is bonded to chlorine (Figure 2.12) due to the presence of Ge-Cl stretching vibrations at ~375 cm⁻¹.⁴⁹ XRF analysis further supports this, as there is approximately an order of magnitude decrease in the chlorine intensity after annealing at 375 °C. Furthermore, it has been reported in previous temperature-programmed desorption studies that Cl desorbs off of germanium at temperatures ranging from 300 to 350 °C.⁵₀ However, there is a significant change in the absorption spectrum when annealing at temperatures above 75 °C. The absorption onset, as detected by DRA, red shifts by 0.06 eV upon annealing at 75 °C (Figure 2.11b). The absorption profile continues to red-shift with higher temperature annealing until 250 °C, when the absorption onset (0.58 eV) goes below that of bulk germanium (0.67 eV). Previously studies have reported that amorphous Ge thin films have band gaps lower than that of bulk germanium (0.50 vs 0.67 eV)⁵¹ and amorphous hydrogenated germanium films have larger band gaps (1.1 eV)⁵². There is no obvious change in the XRD patterns (Figure 2.11c) until 150 °C, at which point the c-axis decreases from 11.04 Å to 10.70 Å and the FWHM of this (002) reflection decreases from 1.3° to 0.8° in 2θ. The diffraction pattern shows complete amorphization upon annealing at 175 °C. Raman spectroscopy shows a consistent decrease in the intensity of both out of plane (A₁) and in plane (E₂) modes as a function of annealing temperature (Figure 2.11d). After 175 °C, there is ~2 order magnitude decrease in the Raman scattering intensity of both modes. Taken together, this
suggests that amorphization occurs at temperatures (~75 °C) well below that of dehydrogenation temperature (200-250 °C).

**Figure 2.** Thermal stability of GeH. (a) TGA analysis of GeH. (b) DRA spectra, (c) XRD patterns, and (d) Raman spectra of GeH measured after four hours’ annealing at various temperatures under 5% H₂ in Ar. In (c) the starred peaks correspond to reflections of an internal Ge standard, and the dashed line is drawn to guide the eye.
Figure 2. 12 FTIR of GeH in the far IR range.

Since PDF measurements does not require periodic lattice and can detect amorphization features, the temperature-dependent PDF measurements can provide more evidence of the amorphization process than XRD. Upon annealing, the scattering between GeH's in-plane Ge-Ge pairs decreases gradually, which coincides with an increase in scattering of Ge-Ge pairs at 5.7 Å, 7.4 Å, and 9.0 Å (Figure 2.13a). These distances correspond to the interlayer Ge–Ge interactions that occur in crystalline Ge and not in GeH. Both the drop off in GeH's Ge–Ge scattering, and the emergence of these new scattering peaks, start at temperatures between 75 and 100 °C, and start to change more significantly between 100 and 125 °C (Figure 2.12a, inset). A more direct signature of amorphization is the disappearance of scattering peaks at high-r values. However, the
5% crystalline Ge impurity prevents us from comparing the relative changes in the high-r and low-r range of the raw data.\textsuperscript{22,53} Therefore, we subtracted the partial PDF pattern of crystalline Ge from the temperature dependent PDF data by rescaling the room temperature crystalline Ge PDF to match the amplitude of features above 28 Å of the variable temperature PDF.\textsuperscript{27} The Ge-subtracted difference curves at room temperature and 205 °C are plotted for comparison (Figure 2.13b). Only scattering features at low-r (1–15 Å) remain in 205 °C PDF, indicative of amorphization. All together, the temperature dependent PDF confirms that germanane amorphization occurs at significantly lower temperatures than the 200–250 °C dehydrogenation temperature.
Figure 2. 13 Temperature-dependent PDFs. (a) Temperature-dependent PDF of GeH from room temperature (purple) to 250 °C (red). The data are truncated at 10 Å to highlight the differences. Inset is the ratio of the intensity of different peaks (arrowed) to the peak at 4 Å. The color of the arrows correspond to the color of the curve in the inset. (d) Difference curve of PDF at room temperature and 205 °C after subtracting crystalline Ge phase, representing the true features coming from GeH.

To study if the low temperature amorphization is due to the presence of residual trace percentage of Ge-Cl in GeH, we synthesized different versions of GeH with different acids, at different temperatures. Though a few percent of halides are always present in samples prepared from HX (X = Cl, Br, I), no carbonyl vibrational mode was detect in the FTIR measurement in the range of 1600-1800 cm⁻¹ (Figure 2.14). Since DRA is the most sensitive method to detect the thermal amorphization, temperature-dependent DRA measurements were performed on all the GeH samples. A similar temperature dependent red shift in the DRA spectra, with a 75 °C amorphization onset,
was observed for all of them, regardless of acid treatment conditions (Figure 2.15). This evidence nullifies the hypothesis that low-temperature amorphization is caused by Ge-Cl, and confirms that GeH intrinsically amorphizes upon annealing, independent of the chemical identity of trace impurities.

Figure 2.14 FTIR of GeH made from acetic acid.
Figure 2. 15 Temperature-dependent DRA of different GeH samples. The GeH samples were synthesized from concentrated HCl at -40 °C (a), acetic acid at room temperature (b), concentrated HBr at -10 °C (c), concentrated HI at -40 °C (d), concentrated HCl at room temperature (e), and 1.6 M HCl at room temperature (f).
2.4 Conclusion

In summary, we have created gram-scale, millimeter-sized crystallites of hydrogen-terminated germanane (GeH) and have characterized for the first time their long-term resistance to oxidation and thermal stability, a necessary prerequisite for any practical application. PDF measurements were also used to directly derive of the hexagonal two-dimensional puckered graphane-like framework of germanane. The temperature-dependent PDF data directly confirms that germanane amorphizes upon the increasing of temperature. Additionally, we have confirmed that the thermally-induced amorphization onset is inherent to the germanane material and cannot be attributed to the identity of a particular impurity. Theory predicts that GeH has a direct band gap of 1.56 eV with low effective masses, thus strongly increasing the already high carrier mobilities found in Ge without the penalty of the low bulk gap. This notion of creating dimensionally reduced molecular-scale “allotropes” of materials with fundamentally different and potentially transformative properties compared to the bulk can be clearly expanded beyond carbon.

2.5 References for Chapter 2


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3.1 Introduction

Recent research on two-dimensional (2D) materials has shown the significant role of the immediate environment on the properties and reactivity of these van der Waals layers. This suggests, on the other hand, the intriguing possibility of manipulating the properties of single-atom thick materials by covalent termination with rationally designed substituents. For example, a quantum spin Hall state with a surface-tunable spin-orbit gap has been recently predicted for 2D Sn graphene analogues that are terminated with halides but not with hydrogen, opening the door for novel lateral heterostructures between topological and conventional states. Furthermore, researchers have recently developed layered van der Waals systems in which each surface atom requires a covalent ligand to become coordinatively saturated, such as MXenes, the amine coordinated II–VI chalcogenides, and the group IV graphene analogues such as silicane or germanane. Because the valence/conduction bands of these materials are comprised of metal–metal or metal–anion bonding within the 2D plane, rather than the p-bands such as that in graphene, these systems offer the possibility to tune the entire electronic properties on the
basis of the identity and electron withdrawing capability of the substituent, without completely disrupting the relevant electronic states. Therefore, developing a general synthetic approach to graft different organic ligands to the 2D layers will help to develop the understanding of ligand influence on properties beside theory predictions.

In this chapter, we demonstrate a facile, one-step metathesis approach that directly converts CaGe2 crystals into mm-sized crystals of methyl-terminated germanane (GeCH₃). Replacing –H termination in GeH with –CH₃ increases the band gap by ~ 0.1 eV to 1.7 eV, and produces band edge fluorescence with a quantum yield of ~ 0.2%, with little dependence on layer thickness. Furthermore, the thermal stability of GeCH₃ has been increased to 250 °C compared with 75 °C for GeH. This one-step metathesis approach should be applicable for accessing new families of two-dimensional van der Waals lattices that feature precise organic terminations and with enhanced optoelectronic properties.

3.2 Experimental

3.2.1 Materials

Iodomethane and isopropanol were obtained from Sigma-Aldrich and used without further purification. Aqueous HCl was obtained from Fisher Scientific and used without any further purification. Water used here was purified with Milli-Q Reference from Millipore.

3.2.2 Sample Synthesis and Preparation

To synthesize GeCH₃, the CaGe₂ crystals were loaded into an extraction thimble, fully immersed in iodomethane, with a separated distilled water phase outside in the
beaker and stir bar at the bottom of the extraction thimble (Figure 3.1). The reaction was running at room temperature for around a week. After the reaction, those exfoliated flakes were rinsed with isopropanol, concentrated HCl (aq) followed by isopropanol. The sample was then dried on a Schlenk line at room temperature.

![Figure 3.1 Picture of bi-phase CH₃I/H₂O reaction setup.](image)

**Figure 3.1 Picture of bi-phase CH₃I/H₂O reaction setup.** The CaGe₂ crystals are loaded into an extraction thimble, fully immersed in CH₃I, while the byproduct, CaI₂, is transferred into the H₂O region in the beaker.

For all thermal stability study, the room temperature sample was annealed at different temperatures under the flow of 5% H₂ in Ar, then cooled down and characterized at room temperature.
To study the photoluminescence (PL) intensity of GeCH₃ flakes with different thickness. The bulk GeCH₃ flakes were exfoliated onto 285 nm SiO₂/Si substrate with kapton tape. The tape residue was cleaned with acetone and then with isopropanol, followed by a N₂ blow dry to clean the residue solvent on the substrate.

3.2.3 Instrumentation

Powder X-ray diffraction (XRD) (Bruker D8 powder X-ray diffractometer, Rigaku MiniFlexII X-Ray diffractometer) and single-crystal XRD (Nonius Kappa CCD diffractometer) were used to study the structure of GeCH₃. Fourier transform infrared spectroscopy (FTIR) measurements were collected on a Perkin-Elmer Frontier Dual-Range FIR/MidIR spectrometer that was loaded in an Ar-filled glovebox. X-ray photoelectron spectroscopy (XPS) was collected using a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a monochromated (Al) X-ray gun. The atomic force microscopy (AFM) images were collected on a Bruker AXS Dimension Icon Atomic/Magnetic Force Microscope with Scan Asyst. Diffuse reflectance absorption (DRA) (Perkin-Elmer Lambda950 UV/Vis Spectrometer) and PL (Cary Eclipse Fluorescence Spectrophotometer) measurements were conducted to study the optical properties of the bulk solid crystals. In the PL measurements, the excitation wavelength was set to 380 nm, the excitation and emission slit widths were set to 20 nm and 5 nm, respectively. The absolute quantum yield of the solid samples was measured with the Quanta-phi (HORIBA Scientific) assembled in Fluorolog (HORIBA Scientific).

The temperature-dependent and the thickness-dependent PL measurements were collected on exfoliated flakes, using a Renishaw InVia Raman equipped with a CCD
detector upon excitation of a 633 nm HeNe laser at a power density of ~24 mW/cm², with a laser spot size of ~2 mm diameter. The thicknesses of these flakes were measured by AFM to identify exfoliated flakes that had regions of relatively uniform thickness larger than the excitation spot size. The weighted average height from the AFM measurement was used to determine the thickness. For the temperature-dependent PL, exfoliated flakes were annealed at different temperatures under the flow of 5% H₂ in Ar in situ, and their PL was recollected on the same flake after cooling down to room temperature. The same trend was observed for three different exfoliated flakes. Thermogravimetric Analysis (TGA) using Q-500 thermogravimetric analyzer, was collected at the ramping rate of 10 °C/min and under the flowing of N₂ at the rate of 50 ml/min. Elemental Analysis (Atlantic Microlab Inc) of the C/H ratio was collected to determine the ratio of CH₃-termination to H-termination.

3.3 Results and Discussion

3.3.1 Structural Characterization

Since our trials on the functionalization of GeH turned out to be unsuccessful due to the amorphization of GeH upon radical reaction, we looked back into the starting material, CaGe₂, and tried to do methylation directly on it with methylation reagent like CH₃I. We hypothesized that the anionic Ge⁻ on the surface and edges of the crystals could react topotactically in an S_N2 or metathesis-like fashion with CH₃I, to form a Ge-CH₃ bond along with CaI₂ byproduct. The expansion of the lattice would allow the precursors to diffuse inward and the reaction would proceed to completion. However, in our initial experiments with pure CH₃I, only the surface layers of CaGe₂ had reacted, likely due to

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the low solubility of CaI₂. Instead, we developed a bi-phase CH₃I/H₂O solvent reaction in which CaGe₂ crystals are fully immersed in CH₃I, while CaI₂ is transferred into the H₂O layer (Figure 3.1). After rinsing in concentrated HCl to remove any trace residual CaI₂, and then isopropanol, the reaction yields crystals of GeCH₃ that are ~1mm in diameter and ~100 mm in thickness (Figure 3.2b). Single crystal X-ray diffraction analysis (Figure 3.2c) shows that each one of these crystallites is a single crystal having a hexagonal spacing of \( a = 3.96 \) Å; however, the interlayer turbostratic disorder and curvature of these crystallites preclude determination of the \( c \) axis spacing. Similar to GeH, the broad and small number of peaks in the in-house XRD makes it impossible to distinguish the structure between a 2H P6₃mc and a 6R R-3mc unit cell (Figure 3.2d). From the analysis of the XRD pattern, GeCH₃ crystals can be fit to either a 2H unit cell with \( a = 3.97 \) Å and \( c = 17.26 \) Å (8.63 Å per layer) or 6R unit cell with \( a = 3.99 \) Å and \( c = 51.78 \) Å (8.63 Å per layer). This corresponds to an expansion in the \( a \)-direction and a 3.1 Å increase in interlayer spacing compared to GeH,⁶ which has the interlayer spacing of 5.50 Å. This 3.1 Å increase is close to twice the difference between the Ge-C bond length (1.95 Å) and the Ge-H bond length (1.52 Å) plus twice the difference between the van der Waals radii of -CH₃ (2.0 Å) and -H (1.2 Å),¹⁵ further indicating substitution of the -H substituent with a -CH₃ substituent.
Figure 3. 2 The one-step topotactic transformation of CaGe$_2$ into GeCH$_3$ crystals. (a) Schematic illustration of conversion of CaGe$_2$ (left) into GeCH$_3$ (right). (b) Optical images of GeCH$_3$ crystals with select crystals on graph paper with a 1mm grid. (c) Single-crystal XRD pattern of GeCH$_3$ collected down the [001] zone axis. (d) Powder XRD patterns of GeH (blue) and GeCH$_3$ (red). The starred peaks correspond to diffraction reflections of an internal Ge standard. The dotted line highlights the changes in the 100 reflections between GeH and GeCH$_3$. 

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FTIR spectroscopy further confirms the \(-\text{CH}_3\) surface termination in GeCH$_3$ and that our sample is free of residual oxide (Figure 3.3). In GeCH$_3$, the major Ge-H stretching frequency$^6, 16-19$ at \(~2,000\text{ cm}^{-1}\) is almost completely gone and replaced by a Ge-C stretch that occurs at 573 cm$^{-1}$. The other major modes that are observed in GeCH$_3$ correspond to \(-\text{CH}_3\) stretching at 2,907 and 2,974 cm$^{-1}$, \(-\text{CH}_3\) bending at 1,403 and 1,237 cm$^{-1}$ and \(-\text{CH}_3\) rocking at 778 cm$^{-1}$.$^{19, 20}$ The residual amount of Ge-H stretching suggests that there exists a small percentage of \(-\text{H}\) termination, and elemental analysis suggests that 90% $\pm$ 10% of the germanium atoms are terminated with \(-\text{CH}_3\). This residual \(-\text{H}\) could result either from the minor solubility of H$_2$O in CH$_3$I, or during the washing process. To further confirm the identity of each vibrational mode, we also created Ge$^{13}$CH$_3$ and GeCD$_3$. In Ge$^{13}$CH$_3$, the Ge-C stretch shifts down to 558 cm$^{-1}$, and the other \(-\text{CH}_3\) vibrational modes slightly decrease by 1–10 cm$^{-1}$ (Table 3.1). There is a much more significant change in the vibrational energies of GeCD$_3$, as the \(-\text{CD}_3\) stretching modes are shifted to 2,240 and 2,116 cm$^{-1}$, the \(-\text{CD}_3\) bending mode decreases to 1,024 and 954 cm$^{-1}$, the \(-\text{CD}_3\) rocking mode decreases to 584 cm$^{-1}$, and the Ge-CD$_3$ stretch decreases to 530 cm$^{-1}$ (Table 3.1).$^{19}$ As the 778 cm$^{-1}$ \(-\text{CH}_3\) rocking mode can possibly mask the existence of any residual Ge-O-Ge or Ge-O vibrational modes which normally occur from 800–1,000 cm$^{-1}$,$^{16, 18}$ the shift of this rocking mode in GeCD$_3$ allows elucidation of any residual Ge–O–Ge or Ge–O. The only vibrational modes observed in this region for GeCD$_3$ are the 770 and 830 cm$^{-1}$ vibrations that correspond to bond-bending Ge-H$_2$ modes from nearest neighbor Ge atoms at the crystal edges.$^6, 17, 18$
Figure 3. 3 FTIR of GeCH$_3$ with different isotopes. FTIR spectra of GeH (i), GeCH$_3$ (ii), Ge$^{13}$CH$_3$ (iii) and GeCD$_3$ (iv). The intensity of the four spectra are all multiplied by 0.5 in the range of 400–900 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Vibrational Modes*</th>
<th>GeCH$_3$</th>
<th>Ge$^{13}$CH$_3$</th>
<th>GeCD$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$ stretch</td>
<td>2974, 2907</td>
<td>2972, 2902</td>
<td>2240, 2116</td>
</tr>
<tr>
<td>-CH$_3$ bend</td>
<td>1403, 1237</td>
<td>1402, 1230</td>
<td>1024, 954</td>
</tr>
<tr>
<td>-CH$_3$ rock</td>
<td>778</td>
<td>764</td>
<td>584</td>
</tr>
<tr>
<td>Ge-CH$_3$ stretch</td>
<td>573</td>
<td>558</td>
<td>530</td>
</tr>
</tbody>
</table>

Table 3. 1 Comparison of vibrational modes in GeCH$_3$, GeCD$_3$ and Ge$^{13}$CH$_3$.

* Here, C refers to either C or $^{13}$C, H refers to either H or D depending on the isotope listed. The units for all vibrations are in cm$^{-1}$. 

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XPS measurements indicate a single Germanium +1 oxidation state (Figure 3.4), further suggesting that GeO₂ and other surface oxides are not present. The Ge 2p₃/₂ peak occurs at 1,217.5 eV, which is slightly shifted compared with the observed 1,217.8 eV peak in GeH, but consistent with CH₃-terminated Ge (111). This slight shift to lower XPS binding energy is consistent with previously observed XPS spectra of –H or –CH₃ terminated silicon surfaces²¹ due to the more electron donating nature of –CH₃ compared with –H.

![Figure 3. 4 Ge 2p₃/₂ XPS spectra for GeD and GeCH₃.](image)

3.3.2 Optical Properties and Band Structure

The absorption and fluorescence measurements of GeCH₃ are consistent with that of a direct band gap semiconductor. GeCH₃ has strong PL emission centered at 1.7 eV
(730nm (red)), which is close to the observed DRA onset at 1.69 eV (Figure 3.5a). This corresponds to a 0.1 eV increase in band edge compared with GeH (1.59 eV) (Figure 3.5b). Band structure calculations for the measured structure using the hybrid HSE06 exchange-correlation functional, confirm this band gap, and predict that the two-layer unit cell has a direct band gap of 1.82 eV (Figure 3.5c). The red PL can be easily detected by eye under UV illumination in both solid-state samples and in suspension in isopropanol (Figure 3.5d). The full-width at half maximum (FWHM) of the fluorescence emission is ~250 meV. The absolute quantum yield of the solid flakes was measured to be 0.23%. This represents a minimum bound of the quantum yield, due to the difficulty in correcting for self-absorption in solid-state measurements. The FWHM and quantum yield values are close to those observed in exfoliated single-layer MoS2, which are 50–150 meV, and 0.4–0.5%,25,26 respectively. We hypothesize that even further improvements in the quantum yield could arise with better control over the degree of –CH3 versus –H functionalization. In MoS2 and many other metal dichalcogenides, a direct band gap is only observed when exfoliated down to single layers,27 making the preparation of large-area single layers a necessary and challenging requirement before optoelectronic devices can be fabricated. In contrast, we observe that the PL emission intensity of exfoliated samples is linearly proportional to the number of layers from 13–65 layers (Figure 3.5e, 3.6). The band edge emission does not depend on layer thickness, at least with 13 layers and above, reflecting the relatively weak electronic coupling and orbital overlap of the conduction and valence bands in neighboring layers. This is in contrast to the overlap of neighboring C 2pz orbitals in graphite, as well as the S 3pz
orbitals at the G point in MoS$_2$. Finally, the intense PL contrasts with our observations on our previously reported crystals of GeH, of which we have yet to observe any band edge PL. Taking together, this data shows that the nature of the covalently modifiable surface ligand can tune the optoelectronic properties of these materials.
Figure 3.5 The optical properties and band structure of GeCH₃. (a) DRA (red) and PL (blue) of GeCH₃. (b) DRA spectra of GeH (blue) and GeCH₃ (red) plotted in Kubelka-Munk function versus photon energy. (c) Electronic band structure of a bilayer GeCH₃ unit cell calculated using the hybrid HSE06 theory including spin-orbit coupling with experimental lattice parameters (3.96 Å), predicting a 1.82 eV direct band gap. The hole and electron effective masses for each extrema are indicated in red. (d) Images of GeCH₃ photoluminescence of crystals (left) and in suspension in isopropanol (right), upon illumination with a handheld 365 nm light. Scale bars, 1 cm. (e) PL intensity of exfoliated GeCH₃ thin flakes having average thicknesses ranging from 13-65 nm. Inset is the raw PL spectra of flakes with the thickness of 13 nm (wine), 27nm (violet), 29nm (orange), 31 nm (olive), 49nm (magenta) and 65nm (blue).
Figure 3. 6 AFM images and height profiles of exfoliated GeCH₃ flakes. The scale bar in d is in 1μm, and all other scale bars are in 2μm.
Figure 3.6 continued
3.3.3 Thermal Stability

We previously observed that GeH begins to amorphize upon annealing at 75 °C, is completely amorphous above 175 °C and starts to dehydrogenate between 200 °C and 250 °C. In contrast, GeCH$_3$ has considerably enhanced thermal stability. According to TGA, a transition occurs starting at ~300 °C (Figure 3.7a) that corresponds to the expected mass loss for approximately 90% CH$_3$-termination, which is in excellent agreement with our elemental analysis. We have previously found that DRA is a much more sensitive probe of the degree of amorphization than any other technique, due to the reduced band gap of amorphous germanium. In the temperature-dependent DRA, there is virtually no shift in band edge emission up to 200 °C, whereas after annealing at 250 °C and 300 °C, the band edge red-shifts by 0.06 and 0.10 eV, respectively (Figure 3.7b). The powder XRD pattern also shows negligible changes after annealing up to 250 °C, but it is almost completely amorphous after annealing at 300 °C (Figure 3.7c). The intensity of photoluminescence emission also started to decrease after annealing at 250 °C (Figure 3.7d). These techniques collectively demonstrate that GeCH$_3$ begins to amorphize at 250 °C. Considering the lack of any PL in our previous studies on GeH, the enhanced stability upon methyl-termination is likely necessary to realize semiconductor properties such as band edge photoluminescence that are often disrupted by defect states.
Figure 3. 7 The enhanced thermal stability in GeCH$_3$. (a) Thermogravimetric analysis of GeCH$_3$. (b,c) DRA spectra (b) and powder XRD patterns (c) of bulk GeCH$_3$ after annealing in 5% H$_2$ in Ar for four hours at various temperatures. (d) Photoluminescence spectra of a single exfoliated GeCH$_3$ flake using the same annealing procedure.

3.4 Conclusion

In summary, we have created for the first time GeCH$_3$, a covalently modified direct band gap germanane, via a one-step topotactic metathesis reaction of CaGe$_2$ crystals with CH$_3$I. We have shown that covalent methyl surface termination not only
increases the band gap by 0.1 eV, but also enhances the thermal stability compared with GeH. The photoluminescence quantum yield is on the same order of magnitude as other single-layer metal chalcogenides, but does not have the stringent single-layer requirement to observe such band edge emission, making these materials intriguing building blocks for future optoelectronic devices. This topotactic metathesis reaction can be extended to create new families of organic-terminated van der Waals materials from other solid-state crystal structures. Dimensionally reduced atomic-scale derivatives can have dramatically different properties than their parent analogue, which can be tuned with the nature of the surface substituent.

3.5 References for Chapter 3


Chapter 4: Enhanced Methyl Coverage and Stability in GeCH₃ via an Optimized Air-Free Route

4.1 Introduction

In the previous two chapters, we have reported the synthesis of two different ligand-terminated germanium graphane analogues: hydrogen-terminated germanane (GeH) and methyl-terminated germanane (GeCH₃), and found that GeCH₃ is not only more thermal stable than GeH, but also exhibits strong photoluminescence (PL) and features a higher band gap.¹ ² However, the reported GeCH₃ has around 10% hydrogen termination and its air stability is not studied yet. Since 2D materials are very sensitive to the immediate environment,³ ⁸ a small difference like the increase of methyl to hydrogen ratio can potentially further improve the optoelectronic properties in GeCH₃. For instance, simply by treating MoS₂ in organic superacid, its quantum yield increased dramatically from below 1% to 95%.⁹ Furthermore, the previous reaction is a bi-phase reaction, which is exposed to air and water, making it hard to extend the reaction to other very air and/or water sensitive organohalides with potentially interesting functional groups.

To these ends, in this chapter, we first studied the air stability of GeCH₃ synthesized from the previous bi-phase method and found that it is very air sensitive due to the introduced Ge-Cl bond during the HCl treatment step. Then, we developed an
optimized air-free route to achieve higher methyl to hydrogen ratio in GeCH$_3$ (~5% hydrogen). Additionally, we found that at least six equivalents of water is needed during the reaction. Finally we have shown that GeCH$_3$ prepared from this air-free method has improved air and thermal stability, with the bulk sample resilient to air for at least 50 days and the methyl desorption temperature increased by around 75 °C.

4.2 Experimental

4.2.1 Materials

Iodomethane and isopropanol were obtained from Sigma-Aldrich and was used without further purification. Aqueous HCl was obtained from Fisher Scientific and used without any further purification. Water used here was purified with Milli-Q Reference from Millipore. Acetonitrile was also obtained from Sigma-Aldrich and was distilled before use. To distill acetonitrile, CaH$_2$ was first put into acetonitrile and let sit for at least an hour, then the solvent was distilled into dried molecular sieve at atmosphere press. The distilled solvent was then bubbled with Ar gas for 20 mins.

4.2.2 Sample Synthesis and Preparation

In the bi-phase method, the CaGe$_2$ crystals were loaded into an extraction thimble, fully immersed in iodomethane, with a separated distilled water phase outside in the beaker and stir bar at the bottom of the extraction thimble. The reaction was running at room temperature for around a week. After the reaction, those exfoliated flakes were rinsed with isopropanol, concentrated HCl (aq) followed by isopropanol. The sample was then dried on a Schlenk line at room temperature.
In the optimized synthetic route, CaGe₂ crystals were first loaded into an air-free flask inside the glovebox. The flask was then connected to the Schlenk line, where all the joints are evacuated and filled with Ar for three times. Liquid reagents including iodomethane, acetonitrile and water were then added into the flask under flowing Ar. In a typical reaction, the molar ratios of CaGe₂:CH₃I:H₂O were controlled at 1:30:10 while CH₃CN was used as a solvent. The reaction was run at room temperature for around a week. Reactions with different CaGe₂ to water molecular ratios were also conducted with the same number of equivalents of iodomethane and acetonitrile, as this ratio was found to be critical for the reaction to initialize and to complete. For purification, the suspension was washed with distilled acetonitrile inside a glovebag and then dried on a Schlenk line. For thermogravimetric analysis (TGA) and elemental analysis, samples were evacuated at 80 °C for three hours on a Schlenk line to get rid of any absorbed water or solvent.

4.2.3 Instrumentation

Powder X-ray diffraction (XRD) (Bruker D8 powder X-ray diffractometer, Rigaku MiniFlexII X-Ray diffractometer) was used to study the structure of GeCH₃. Fourier transform infrared spectroscopy (FTIR) measurements were collected on a Perkin-Elmer Frontier Dual-Range FIR/MidIR spectrometer that was loaded in an Ar-filled glovebox. X-ray photoelectron spectroscopy (XPS) was collected using a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a monochromated (Al) X-ray gun and Ar ion was used for etching. Diffuse reflectance absorption (DRA) measurements (Perkin-Elmer Lambda950 UV/Vis Spectrometer) and photoluminescence (PL) (Cary Eclipse Fluorescence Spectrophotometer) measurements were conducted to
study the optical properties of the bulk solid crystals. In the photoluminescence (PL) measurements, the excitation wavelength was set to 380 nm, the excitation and emission slit widths were set to 20 nm and 5 nm, respectively. TGA (Q-500 thermogravimetric analyzer) was collected under flowing N₂ with the rate at 10 °C/min. Elemental Analysis (Galbraith Laboratories, Inc.) of the C/H ratio was collected to determine the ratio of CH₃-termination to H-termination in the products.

4.3 Results and Discussion

4.3.1 Air Stability of GeCH₃ Synthesized from Bi-Phase Method

The starting material, CaGe₂, is well known to be very air sensitive. Though it was protected from air and water with CH₃I during the previous bi-phase reaction, a small amount of water and oxygen can always dissolve into the CH₃I layer and oxidize the structure. Consequently, we found that the as-obtained GeCH₃ is already oxidized, with features like a shoulder on the –CH₃ rocking mode in the range of 800-1000 cm⁻¹ in the FTIR spectrum (Figure 4.1a), indicating Ge-O bonding. HCl treatment was then followed to wash away residual germanium oxides (GeOₓ). After this HCl treatment, the Ge-O stretching shoulder disappears, indicating that the GeOₓ are gone. However, since the Ge-O stretching mode is so close to the strong –CH₃ rocking at 770 cm⁻¹, it is ambiguous to determine the presence of Ge-O vibration just based on the appearance of a shoulder peak. To separate the Ge-O stretching mode from –CH₃ rocking modes and clearly demonstrate the appearance and disappearance of GeOₓ, we collected the same series of FTIR spectra with GeCD₃ (Figure 4.1b). In the as-obtained GeCD₃, it is obvious that germanium is partially oxidized with a broad Ge-O stretching mode between 800 and...
1000 cm$^{-1}$. After HCl washing, this single broad peak is gone and replaced with a doublet which can be assigned to a Ge-H$_2$ bending mode as previously reported in GeH.$^1$ However, after exposure to air for a day, the Ge-O stretching mode appears again in both GeCH$_3$ and GeCD$_3$ (Figure 4.1).
Figure 4.1 FTIR of bi-phase GeCH₃ (a) and GeCD₃ (b) collected before (blue) and after HCl treatment (red), along with after HCl treatment and exposure to air for a day (green).
The surface oxidization states of both the before and after HCl treatment samples were then studied by XPS (Figure 4.2). The as-obtained bi-phase GeCH$_3$ shows a mixture of different oxidation states of Ge$^+$ (1217.6 eV) and Ge$^{2+/3+}$ (1219.4 eV), indicating that the surface of these flakes are oxidized (Figure 4.2b). After HCl treatment, only a single peak was observed at 1217.5 eV, which is indicative of Ge$^+$, confirming that the surface GeO$_x$ are removed with HCl (Figure 4.2b). Additionally, upon exposure to air for three days, a Ge$^{2+/3+}$ shoulder emerges at $\sim$1219.9 eV with a percentage of 35.6%, which was calculated by applying a standard Gaussian fit. Consequently, although oxygen-free GeCH$_3$ is obtained after HCl treatment, both the surface and the bulk of GeCH$_3$ are not stable in air over time, surprisingly in contrast to the previous studies on alkyl-terminated Ge (111) surfaces which are reported to be stable in air for several days.$^{12, 13}$

Figure 4.2 (a) Survey and (b) Ge 2p$_{3/2}$ XPS of bi-phase GeCH$_3$ collected before (blue) and after HCl treatment (red), along with after HCl treatment and exposure to air for a day (green).
To further understand the cause of the oxidization, we exposed the as-obtained bi-phase GeCH$_3$ to air for various time periods and collected the FTIR on them. It was found that the Ge-O stretching shoulder did not change over a time of 26 days (Figure 4.3), indicating that Ge-C bonds are inert to air. Both the survey and Cl 2p XPS spectra indicate that Cl element was introduced into the sample during the HCl treatment (Figure 4.2a, 4.4a). To confirm that the Cl is bond to Ge, we then collected the FTIR spectrum of GeCH$_3$ before and after HCl treatment in the far IR range and found the emergence of Ge-Cl stretching vibrational mode in the sample after HCl treatment at around 375 cm$^{-1}$ (Figure 4.4b), which is in agreement with the previous reported Ge-Cl vibrational mode.\textsuperscript{14} Furthermore, the immersing of oxidized Ge (111) wafer into aqueous HCl is known as a standard approach to obtain Cl-terminated Ge (111) surface.\textsuperscript{15}
Figure 4. 3  Time-dependent FTIR of as-obtained bi-phase GeCH$_3$.

Figure 4. 4 (a) Cl 2p XPS spectra and (b) FTIR (far IR range) of bi-phase GeCH$_3$ collected before (blue) and after HCl treatment (red).
We have summarized the reaction scheme that happened on bi-phase GeCH₃ in Figure 4.5. During the topotactic deintercalation, due to the water sensitivity of CaGe₂, the bi-phase reaction (Figure 4.5, top right) will produce the as-obtained GeCH₃ with partial hydroxide termination (Ge(CH₃)₁₋ₓ(OH)ₓ), which will not further oxidize in air since the Ge-C bond is air stable. The HCl washing successfully replaces those hydroxide ligands with chlorine, resulting in Ge(CH₃)₁₋ₓClₓ. However, the Ge-Cl bonds make those post-HCl samples air sensitive. Upon exposure to air, Ge-Cl is oxidized, yielding Ge(CH₃)₁₋ₓ(OH)ₓ again.
Figure 4.5 Reactions happened in bi-phase GeCH$_3$ under different conditions. In these crystal structures, yellow, blue, black, gray, red and green spheres refer to calcium, germanium, carbon, hydrogen, oxygen, and chlorine atoms, respectively.

Besides FTIR and XPS, the observed PL in GeCH$_3$ is also very sensitive to oxidization (Figure 4.6). The as-obtained bi-phase GeCH$_3$ has a PL at 1.90 eV with a shoulder at around 1.76 eV, both of which are much higher than the reported band gap
absorption of GeCH$_3$ at around 1.7 eV. After the HCl treatment, a single asymmetric PL peak was observed at 1.7 eV with a full-width-at-half-maximum (FWHM) of ~250 meV. However, after one day’s air exposure, PL blue shifts back to 1.87 eV with a shoulder at 1.76 eV, in the similar positions with the one before HCl treatment. Combining with the observed changes in FTIR and XPS, we can conclude that the PL of GeCH$_3$ is also dependent on the oxidization states of germanium as PL blue shifts when germanium oxidizes.

Figure 4.6  PL of bi-phase GeCH$_3$ collected before (blue) and after HCl treatment (red), along with after HCl treatment and exposure to air for a day (green).
4.3.2 Reaction Optimization

With the above conclusions in mind, we hypothesized that an air and water free synthetic route would produce oxygen-free GeCH₃, which would be air stable since no Ge-Cl will present. Additionally, to get higher methyl coverage, the hydrogen source, water, should be avoided or at least minimized. Towards these ends, we first tried to run the reaction both air and water free using distilled acetonitrile as the solvent. Unfortunately, no reaction was observed after a week with no appearance of –CH₃ vibrational modes in FTIR and only CaGe₂ diffraction observed in the XRD pattern.

While keeping the reaction air-free, we then started to adjust the water to CaGe₂ ratio and found that water is actually essential during the reaction (Table 4.1). With 0-2 equivalents of water to CaGe₂, no sign of reaction was observed after a week. When the amount of water was increased to 4 equivalents, the methylation starts to happen with the emergence of –CH₃ vibrational modes and Ge-C stretching mode in FTIR (Figure 4.7a). Additionally, a new peak in the XRD pattern was observed at around 8 Å with a d-spacing of 1 nm (Figure 4.7b), the same interlayer spacing in the bi-phase GeCH₃ before HCl treatment. However, with such small amount of water, the reaction is not complete even after a month, which is confirmed by the residual CaGe₂ phase in XRD (Figure 4.7b). With a larger amount of water (H₂O:CaGe₂ ≥ 6), the reaction was complete in a week, similar to the reaction time needed in the bi-phase method where water was used as the solvent. To find out why water is necessary during the reaction, we first tested the solubility of the by-product, CaI₂, in the distilled acetonitrile and found that more than five times of the produced CaI₂ could be dissolved in the amount of acetonitrile that was
added into the reaction. Therefore, the solubility of CaI₂ in acetonitrile is not the limitation of the reaction. The next hypothesis is that water is needed to coordinate with the Ca²⁺ ions between the layers to weaken the ionic bonding between Ca²⁺ ions and Ge⁻ framework, and to move the Ca²⁺ ions out from the lattices. The hypothesis also explains why at least 6 equivalents of water are needed since the most common coordination number of water with Ca²⁺ was found to be 6-8.¹⁶ Additionally, we performed reactions replacing the water with other Ca²⁺ chelating molecules including EDTA (ethylenediaminetetraacetic acid) and crown ether (18-crown-6). However, the CaGe₂ remained completely unreacted after a week.

<table>
<thead>
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<th>H₂O:CaGe₂ ratio</th>
<th>Reaction Status</th>
</tr>
</thead>
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<td>0</td>
<td>No reaction after a week.</td>
</tr>
<tr>
<td>2</td>
<td>No reaction after a week.</td>
</tr>
<tr>
<td>4</td>
<td>Reacted to some extent, but reaction is not complete in a month.</td>
</tr>
<tr>
<td>6</td>
<td>Reaction is complete in a week.</td>
</tr>
<tr>
<td>10</td>
<td>Reaction is complete in a week.</td>
</tr>
</tbody>
</table>

Table 4. 1 Water to CaGe₂ ratio vs. reaction status.
Figure 4. 7 (a) FTIR and (b) XRD of uncomplete reaction between CaGe₂ and CH₃I with four equivalents of water. The starred peaks in (b) are from CaGe₂ phase while the dotted peaks are from GeCH₃ phase. The unlabeled peak is from an internal germanium standard.

4.3.3 Characterization of GeCH₃ from the Optimized Method

Spectroscopy like FTIR, XPS, DRA and PL were collected on the as-obtained GeCH₃ from this optimized method and compared with previous HCl treated GeCH₃ (Figure 4.8, 4.9). All spectra show similar features between both samples, with no Ge-O stretching mode observed in FTIR, a single Ge⁺ peak appeared at 1217.5 eV in the XPS and the same absorption onset and PL peak position, confirming that GeCH₃ synthesized from this air-free method is oxygen-free and behaves similarly with the bi-phase GeCH₃. Nevertheless, those spectra vary from each other in some details. In FTIR, weaker Ge-H
vibration (~2000 cm\(^{-1}\)) intensity was observed in the air-free GeCH\(_3\) (Figure 4.8a), suggesting a higher methyl to hydrogen termination ratio. This is confirmed by elemental analysis, which yields a methyl coverage of 95±3%. Higher methyl coverage is expected since less hydrogen source is present during the reaction. In the optical property measurements, air-free GeCH\(_3\) has a narrower PL peak (FWHM = 180 meV) and a sharper slope (or more close to the ideal step function of absorption predicted by Tauc-Davis Mott estimates) in the absorption curve (Figure 4.9), both of which are indicative of better sample quality with less defects. The improvement in sample quality is also anticipated since two process that can potentially introduce defects, the oxidization of CaGe\(_2\) upon air exposure and the later HCl treatment, are eliminated in the air-free method. To conclude, with this optimized air-free method, oxygen-free GeCH\(_3\) could be obtained without HCl treatment and it has higher methyl coverage and more narrow FWHM of photoluminescence.
Figure 4. 8 (a) FTIR and (b) Ge 2p3/2 XPS comparison between two GeCH₃ samples.

GeCH₃ samples synthesized from bi-phase method after HCl treatment are shown in red (dashed line) while those from the air-free method are shown in green (solid line).
4.3.4 Air and Thermal Stability of GeCH$_3$ from the Optimized Method

The potential utility of methyl-terminated germananes for any functional device strongly hinges on their air and thermal stability. Previous reports have shown that alkyl-terminated Ge (111) surfaces are stable in air for several days$^{12,13}$ and the bulk GeH is resistant to oxidization of at least two months$^1$. Here, we use FTIR and XPS to probe the presence of Ge-O in the bulk and on the surface of GeCH$_3$ prepared from this optimized air-free method, respectively. After exposure to air for 50 days, No change was observed
in the range of 800-1000 cm\(^{-1}\) (Figure 4.10a), where Ge-O stretching vibrational mode falls\(^{11}\) thus proving that the bulk of GeCH\(_3\) resists oxidation. XPS was measured on pristine sample and after exposure to air for 3 days, 10 days, and 10 days plus etching, respectively (Figure 4.10b), and the percentage of the germanium oxidation state for all spectra was calculated by applying a standard Gaussian fit. After 3 days’ exposure to air, a Ge\(^{2+/3+}\) shoulder emerges at \(\sim 1219.3\) eV (28.3\% Ge\(^{2+/3+}\)), which becomes more intense after 10 days of air exposure (44.2\% Ge\(^{2+/3+}\)). However, after Ar etching the top layer, the Ge\(^{2+/3+}\) almost completely disappears with 19.0\% remaining. Together, the XPS and FTIR suggest that only the surface of GeCH\(_3\) becomes oxidized over time while the bulk is resilient to air, similar to what was observed in GeH\(^1\).

![Figure 4. 10 Air stability of GeCH\(_3\) obtained from air-free method. (a) FTIR and (b) Ge 2p\(_{3/2}\) XPS of GeCH\(_3\) after exposed to air for various time periods.](image-url)
The thermal stability of GeCH$_3$ is also improved with this optimized method. We collected the TGA of GeCH$_3$ synthesized from previous bi-phase method and the optimized air-free method and took the derivatives (DTA, differential thermal analysis) of both spectra (Figure 4.11). From the DTA spectra, it is apparent that the peak of methyl desorption increased from 345 °C in the bi-phase method to 420 °C in the air-free method. The latter desorption temperature is very close to the recent report on atomic flat CH$_3$-terminated Ge (111), where methyl desorption was found between 400-450 °C. Furthermore, the percentage weight loss in TGA also increased from bi-phase GeCH$_3$ to air-free GeCH$_3$, suggesting that 95% of Ge atoms are terminated with –CH$_3$ in the air-free method, matching perfectly with the elemental analysis result.

Figure 4.11 Thermal stability of two GeCH$_3$ samples. TGA (top, left axis) and DTA (bottom, right axis) of GeCH$_3$ synthesized from bi-phase (red) and air-free (green) methods, respectively.
4.4 Conclusion

In summary, we have studied the air stability of GeCH\textsubscript{3} produced from the bi-phase method and found that it is the Ge-Cl bond that is introduced during the HCl treatment that makes GeCH\textsubscript{3} air sensitive. Furthermore, the methylation method has been optimized to an air-free approach and water is found to be essential for the topotactic deintercalation reaction. The resulting GeCH\textsubscript{3} using this new method not only shows higher methyl coverage and more narrow FWHM of photoluminescence, also exhibits greater air and thermal stability. Since there exists a large library of numerous commercially available organohalides, this optimized route can be extended to attach different organic ligands to germanane, or sensing applications where selective sensors could be obtained with specific ligand. More importantly, comparison between germanane grafted with different ligands will allow for systematic understanding of the effects of ligand identity on material properties, which will be discussed in the next chapter.

4.5 References for Chapter 4


Chapter 5: Interplay of Ligand Strain and Electronegativity in Tuning the Electronic Structure of Covalently Functionalized Germanane

5.1 Introduction

As the covalent functionalization of numerous families of 2D materials including the group IVA graphane analogues, the transition metal dichalcogenides, and the MXene phases is starting to be established experimentally and theoretically, a systematic understanding about how and to what extent the electronic structure of a 2D material can be tailored by the identity of the ligand is essential before surface functionalization chemistry can be utilized effectively to rationally tailor properties. Germanane, on the other hand, is an ideal model system for probing this ligand effect. In this single atom-thick puckered honeycomb framework, covalently bonded chemical groups will directly couple to the orbitals comprising conduction and valence bands, facilitating the tuning of electronic structure. Furthermore, the arrangement of Ge atoms in these 2D materials is identical to that of a Ge (111) surface, which has a well-established history of surface functionalization for comparison. Experimentally, we have developed a general route for creating multilayered crystals of organic terminated germanane in the last chapter.

Herein, through the preparation of a library of ligand-functionalized germanane crystals, we establish the influence of ligand size and electronegativity on electronic
structure. We show that nearly uniform ligand termination can only be achieved with small enough functional groups, with larger ligands resulting in partial hydrogen-termination. When there is a homogeneous distribution of different ligands, the band gaps and Raman shifts are dictated by their relative stoichiometry in a pseudo-linear fashion similar to Vegard’s law. Ligands that have a greater size and are more electronegative will expand the Ge-Ge bond length, thereby lowering the band gap. Simply by changing the identity of the organic ligand, the band gap of germanane can be tuned by \( \sim 15\% \), highlighting the power of surface chemistry to manipulate the properties of single-atom thick materials.

5.2 Experimental

5.2.1 Materials

All the organohalides were obtained from either Sigma or Oakwood and were used without further purification. Acetonitrile was also obtained from Sigma and was distilled before use. To distill acetonitrile, \( \text{CaH}_2 \) was first put into acetonitrile and let sit for at least an hour, then the solvent was distilled into dried molecular sieve at 150-200 \( ^\circ\text{C} \), at atmosphere pressure. The distilled solvent was then bubbled with argon for 20 minutes. Aqueous HCl was obtained from Fisher Scientific and used without any further purification. Water was purified with Milli-Q Reference from Millipore.

5.2.2 Sample Synthesis and Preparation

To get various GeR (R: organic ligand), \( \text{CaGe}_2 \) crystals were first loaded into an air-free flask inside the glovebox. The flask was then connected to the Schlenk line, where all the joints are evacuated and back filled with argon for three times. Liquids like
organohalides, acetonitrile and water were then added into the flask under the flowing of argon. The molecular ratio of CaGe₂ to organohalides to water were all controlled at 1:30:10. The reactions were running at room temperature for one to two weeks, depending on the ligand. For purification, the suspension was washed with distilled acetonitrile inside a glovebag and then dried on a Schlenk line, followed by HCl treatment to wash out the salts or solvents that were trapped between the layers. During the HCl treatment, the sample was washed with HCl for three times, followed by acetonitrile or dichloromethane for three times to remove HCl, then the washed sample was dried on a Schlenk line.

To get Ge(CH₃)ₓH₁₋ₓ, CaGe₂ crystals were first loaded into an air-free flask inside the glovebox. The flask was then connected to the Schlenk line, where all the joints are evacuated and back filled with argon for three times. Liquid reagents like organohalides, acetonitrile and diluted HCl were then added into the flask under the flowing of argon. The concentration of HCl was controlled here to control the ratio of –H to –CH₃ termination. The reaction was running at room temperature for around one week. For purification, the suspension was washed with distilled acetonitrile inside a glovebag and then dried on a Schlenk line, followed by HCl washing to remove the salts and small molecules trapped between the layers. During this HCl treatment, the sample was washed with HCl for three times, followed by acetonitrile for three times to remove HCl, then the washed sample was dried on a Schlenk line.
For thermogravimetric analysis (TGA) and elemental analysis, samples were evacuated at 80 °C for three hours on a schlenk line to get rid of any absorbed water or solvent.

5.2.3 Instrumentation

Powder X-ray diffraction (XRD) (Bruker D8 powder X-ray diffractometer, Rigaku MiniFlexII X-Ray diffractometer) was used to study the structure of GeR and Ge(CH\textsubscript{3})\textsubscript{x}H\textsubscript{1-x} samples. Fourier transform infrared spectroscopy (FTIR) were collected on a Perkin-Elmer Frontier Dual-Range FIR/MidIR spectrometer that was loaded in an Ar-filled glovebox. Diffuse reflectance absorption (DRA) measurements (Perkin-Elmer Lambda950 UV/Vis Spectrometer, OceanOptics USB4000) was conducted to study the band gap of the bulk solid crystals. TGA (Q-500 thermogravimetric analyzer) was collected in flowing N\textsubscript{2} at 10 °C/min. Elemental Analysis (Galbraith Laboratories, Inc.) of the C/H ratio was collected to determine the ratio of CH\textsubscript{3}-termination to H-termination for all the GeR.

Raman spectra were collected using a Renishaw InVia Raman equipped with a CCD detector upon excitation using a 633-nm HeNe laser. During the measurement, the photoluminescence is so strong that it will saturate the detector with laser power above 3 \textmu W/cm\textsuperscript{2} on a bare sample. Below this laser power, no Raman vibrational modes were observed on GeH or GeCH\textsubscript{3}. We sealed the sample in a thick capillary and run the Raman measurements on samples inside the capillary and was able to excite the sample with a higher laser power density of \sim 24 mW/cm\textsuperscript{2} and vibrational modes was observed in all GeR.s. The capillary here absorbed partial fluorescence and helped to increase the
maximum of the laser power that could be applied before saturating the detector. At least
ten spectra were collected on each sample at different spots. Each spectrum was fitted
into a function with a mix of 70% Lorentz function and 30% Gaussian function, along
with an asymmetric factor. The average and standard deviation of the peak positions
found in the ten spectra were reported.

5.3 Results and Discussion

5.3.1 Full Coverage Ligands

The first group of organic ligands –CH₃, –CH₂OCH₃, and –CH₂CH=CH₂ can be
grafted onto nearly every single germanium atom in the germanane framework. In the
FTIR spectra of these materials, an intense Ge-C stretching mode occurs at ~570-590
cm⁻¹ for these different spectra while the major Ge-H stretching frequency at 2000 cm⁻¹ is
almost completely gone (Figure 5.1a). As grown, no Ge-O stretching vibrations from
800-1000 cm⁻¹ are observed, indicating a lack of oxidation. The GeCH₃ and GeH FTIR
spectra are fully consistent with our previous isotopic labeling studies. Other
spectroscopic signatures indicate successful grafting of these ligands onto the framework,
such as the -C=C- bending modes at 1626 cm⁻¹, the =CH₂ stretch at 3075 cm⁻¹, the trans
=CH wagging at 990 cm⁻¹, and the =CH₂ wagging at 908 cm⁻¹ for –CH₂CH=CH₂, and all
the other vibrational modes are consistent with the spectroscopic fingerprints of these
functional groups (Table 5.1, 5.2). The degree of functionalization in GeRₓH₁₋ₓ, was
calculated from the C:H ratio measured via elemental analysis (Table 5.3). For these
three ligands, x ranges from 0.95(2)-1.05(7), indicative of nearly complete termination
with the organic ligand.
Figure 5. 1 Characterization of four nearly full functionalized GeR. (a) FTIR, (b) XRD and (c) Raman of GeCH₃ (i, red), GeH (ii, blue), GeCH₂CH=CH₂ (iii, olive) and GeCH₂OCH₃ (iv, orange). The inset in (c) is the scheme of the E₂ vibrational mode of the germanium framework. The starred peaks in (a) refers to Ge-C bond and those in (b) is coming from the internal Ge standard. All the dash lines are drawn for eye guide.
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<th>Frequency (cm(^{-1}))</th>
<th>Vibrational Modes</th>
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<td>3075</td>
<td>=CH(_2) str.</td>
</tr>
<tr>
<td>3000</td>
<td>=CH(_2) str. / =CH str.</td>
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<td>2950</td>
<td>-CH(_2)- str.</td>
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<tr>
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<td>-CH(_2)- str.</td>
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<tr>
<td>2006</td>
<td>Ge-H str.</td>
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<tr>
<td>1819</td>
<td>=CH(_2) wag overtone</td>
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<tr>
<td>1626</td>
<td>C=C str.</td>
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<td>Left shoulder of 1417</td>
<td>-CH(_2)- def.</td>
</tr>
<tr>
<td>1417</td>
<td>=CH(_2) def.</td>
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<tr>
<td>1385</td>
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<tr>
<td>1297</td>
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<tr>
<td>1150</td>
<td>-CH(_2)- twist</td>
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<td>1059</td>
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<td>828</td>
<td>Ge-H(_2) bend</td>
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<td>762</td>
<td>-CH(_2)- rock</td>
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<td>590</td>
<td>“cis” =CH wag/ Ge-C str.</td>
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<td>“cis” =CH wag/ Ge-C str.</td>
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<tr>
<td>470</td>
<td>“cis” =CH wag</td>
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Table 5. 1 Vibrational modes in GeCH\(_2\)CH=CH\(_2\)

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<td>-CH(_3) def. overtone</td>
</tr>
<tr>
<td>1456, 1437</td>
<td>-C-H def.</td>
</tr>
<tr>
<td>1418, 1390, 1368</td>
<td>-CH(_2)- wag</td>
</tr>
<tr>
<td>1256</td>
<td>-CH(_2)- twist</td>
</tr>
<tr>
<td>1210</td>
<td>-CH(_3) rock</td>
</tr>
<tr>
<td>1148, 1084, 1004, 920</td>
<td>COC str.</td>
</tr>
<tr>
<td>779</td>
<td>-CH(_2)- rock</td>
</tr>
<tr>
<td>572</td>
<td>Ge-C str.</td>
</tr>
</tbody>
</table>

Table 5. 2 Vibrational modes in GeCH\(_2\)OCH\(_3\)
<table>
<thead>
<tr>
<th>R ligand in GeRₓH₁₋ₓ</th>
<th>C (wt %)</th>
<th>C (wt %)</th>
<th>Residual mass (wt %)</th>
<th>fraction of organic coverage x</th>
<th>Expected residual Mass (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>13.02(5)</td>
<td>3.34(1)</td>
<td>83.64(6)</td>
<td>0.95(2)</td>
<td>83.6(3)</td>
</tr>
<tr>
<td>-CH₂CH₃</td>
<td>16.2(4)</td>
<td>3.7(2)</td>
<td>80.1(6)</td>
<td>0.69(8)</td>
<td>78(2)</td>
</tr>
<tr>
<td>-(CH₂)₂CH₃</td>
<td>15.6(3)</td>
<td>3.59(8)</td>
<td>80.8(4)</td>
<td>0.50(5)</td>
<td>78(2)</td>
</tr>
<tr>
<td>-(CH₂)₃CH₃</td>
<td>11.8(3)</td>
<td>2.71(4)</td>
<td>85.5(3)</td>
<td>0.339(14)</td>
<td>78.4(7)</td>
</tr>
<tr>
<td>-(CH₂)₆CH₃</td>
<td>34.1(1.4)</td>
<td>6.4(2)</td>
<td>59.5(1.6)</td>
<td>0.60(9)</td>
<td>55(4)</td>
</tr>
<tr>
<td>-CH(CH₃)CH₂CH₃</td>
<td>6.68(5)</td>
<td>2.09(14)</td>
<td>91.2(2)</td>
<td>0.14(2)</td>
<td>88.8(1.2)</td>
</tr>
<tr>
<td>CH₃I</td>
<td>4.47(12)</td>
<td>1.01(3)</td>
<td>94.52(15)</td>
<td>0.591(8)</td>
<td>94.4(1.3)</td>
</tr>
<tr>
<td>CH₂CF₃</td>
<td>4.06(4)</td>
<td>1.00(9)</td>
<td>94.94(13)</td>
<td>0.21(2)</td>
<td>93(3)</td>
</tr>
<tr>
<td>CH₂OCH₃</td>
<td>20.06(8)</td>
<td>4.0(3)</td>
<td>75.9(4)</td>
<td>1.05(7)</td>
<td>75(7)</td>
</tr>
<tr>
<td>CH₂CH=CH₂</td>
<td>31.4(2)</td>
<td>4.29(16)</td>
<td>64.3(4)</td>
<td>1.02(3)</td>
<td>63.3(7)</td>
</tr>
<tr>
<td>CH₂C₆H₅</td>
<td>18.6(2)</td>
<td>2.1(2)</td>
<td>79.3(4)</td>
<td>0.29(7)</td>
<td>73(5)</td>
</tr>
</tbody>
</table>

Table 5.3 Fraction of organic functionalization (x*) in GeRₓH₁₋ₓ.

* x was calculated from elemental analysis measurements, assuming excess equivalents of –H are terminated on the germanane framework. For allyl and dimethyl ether termination, that have slightly higher C:H ratios than expected for full coverage, x was calculated by the molecular ratio between ligand numbers calculated from carbon and hydrogen, respectively.

The change in lattice parameters after deintercalation are also indicative of covalent termination. The starting material, β-CaGe₂ crystallizes into a 6-layer R-3m crystal structure. After covalent termination with –H/-CH₃, peak broadening and small number (3-5) of reflections in the XRD make it impossible to unambiguously assign the resulting layered structures between a 2H 2-layer hexagonal unit cell or a 6R 6-layer Rhombohedral unit cell. Functionalization with other ligands requires a further reduction of P1 triclinic unit cell symmetry. No matter what the resulting space group is, the first
diffraction reflection corresponds to the interlayer spacing. The interlayer spacing
increases with ligand length, and is within 1-2 Å of the value expected if each ligand is
fully extended and oriented parallel to the c-axis (Table 5.4). The a-lattice parameter of
the honeycomb framework was determined from second major reflection, and calculated
assuming it was either a 2H (100) reflection or a 6R (012) reflection, and increases from
GeH < GeCH2CH=CH2 < GeCH3 < GeCH2OCH3 (Figure 5.1b, Table 5.5). However, in
the Raman spectra, the shift of the E2 mode, corresponding to the in-plane Ge-Ge
framework vibration, increases from GeCH3 > GeH > GeCH2CH=CH2 > GeCH2OCH3
(Figure 5.1c, Table 5.6). The energy of the Raman shift is not correlated to the a-lattice
parameter, due to the possibility for the 2D framework to buckle and produce different
Ge-Ge-Ge bond angles. For example, by keeping the Ge-Ge bond length at a constant
2.43 Å, changing the Ge-Ge-Ge bond angle by just 3 degrees from 109° to 106° can result
in a change in a-lattice parameter that varies from 3.96 to 3.88 Å (Table 5.7).
Consequently, the Raman energy of the E2 vibrational mode serves as a much more direct
readout of the Ge-Ge bond length when comparing different ligands.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Experimental* (Å)</th>
<th>Expected interlayer spacing* (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>5.5</td>
<td>NA</td>
</tr>
<tr>
<td>CH₃</td>
<td>8.6</td>
<td>8.0</td>
</tr>
<tr>
<td>CH₂CH₃</td>
<td>10.4</td>
<td>9.0</td>
</tr>
<tr>
<td>(CH₂)₂CH₃</td>
<td>13.1</td>
<td>12.0</td>
</tr>
<tr>
<td>(CH₂)₃CH₃</td>
<td>13.8</td>
<td>13.0</td>
</tr>
<tr>
<td>(CH₂)₆CH₃</td>
<td>18.0</td>
<td>20.1</td>
</tr>
<tr>
<td>CH(CH₃)CH₂CH₃</td>
<td>13.0</td>
<td>12.0</td>
</tr>
<tr>
<td>CH₂I</td>
<td>10.6</td>
<td>9.7</td>
</tr>
<tr>
<td>CH₂OCH₃</td>
<td>10.9</td>
<td>11.7</td>
</tr>
<tr>
<td>CH₂CH=CH₂</td>
<td>12.2</td>
<td>11.3</td>
</tr>
<tr>
<td>CH₂C₆H₅</td>
<td>12.9</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Table 5.4 Interlayer spacing between germanium layers in GeRₓH₁₋ₓ.

* Experimental values are determined from X-ray diffraction. Expected values are calculated from the difference between Ge-H and Ge-C bond plus the height difference between hydrogen and other ligands, assuming the ligands are fully extended and oriented parallel to the c-axis.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>2H (P6₃mc) (Å)</th>
<th>6R (R-3m) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>3.96(3)</td>
<td>3.99(3)</td>
</tr>
<tr>
<td>CH₂CH₃</td>
<td>3.93(4)</td>
<td>3.95(4)</td>
</tr>
<tr>
<td>(CH₂)₂CH₃</td>
<td>3.94(4)</td>
<td>3.96(4)</td>
</tr>
<tr>
<td>(CH₂)₃CH₃</td>
<td>3.92(6)</td>
<td>3.94(6)</td>
</tr>
<tr>
<td>(CH₂)₆CH₃</td>
<td>3.92(5)</td>
<td>3.93(5)</td>
</tr>
<tr>
<td>CH(CH₃)CH₂CH₃</td>
<td>3.89(5)</td>
<td>3.90(5)</td>
</tr>
<tr>
<td>CH₂I</td>
<td>3.92(8)</td>
<td>3.93(8)</td>
</tr>
<tr>
<td>CH₂OCH₃</td>
<td>4.00(7)</td>
<td>4.03(7)</td>
</tr>
<tr>
<td>CH₂CH=CH₂</td>
<td>3.94(7)</td>
<td>3.96(7)</td>
</tr>
<tr>
<td>CH₂C₆H₅</td>
<td>3.91(5)</td>
<td>3.93(5)</td>
</tr>
</tbody>
</table>

Table 5.5 a-lattice parameter of GeRₓH₁₋ₓ. The results were calculated from two-layer (P6₃mc) or six-layer (R-3m) per unit cell, separately. The uncertainty was calculated from FWHM of the (100) peak in P6₃mc or (012) in R-3m.
Table 5.6 Raman shift of four nearly full functionalized germanane.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Raman Shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>301.6(2)</td>
</tr>
<tr>
<td>CH₃</td>
<td>303.3(3)</td>
</tr>
<tr>
<td>CH₂OCH₃</td>
<td>299.4(5)</td>
</tr>
<tr>
<td>CH₂CH=CH₂</td>
<td>300.6(4)</td>
</tr>
</tbody>
</table>

Table 5.7 Relationship* between bond angle, bond length and a-lattice parameter.

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>θ (°)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.43</td>
<td>109</td>
<td>3.96</td>
</tr>
<tr>
<td>2.43</td>
<td>106</td>
<td>3.88</td>
</tr>
<tr>
<td>2.45</td>
<td>109</td>
<td>3.99</td>
</tr>
<tr>
<td>2.45</td>
<td>106</td>
<td>3.91</td>
</tr>
</tbody>
</table>

* From the structure, the relationship can be expressed as \( \cos \theta = 1 - a^2 / 2d^2 \), where \( \theta \) is the Ge-Ge-Ge bond angle, \( a \) is the a-lattice parameter, and \( d \) is the Ge-Ge bond length.

5.3.2 Larger Ligands

Many other ligand functionalized germanane materials were prepared to further probe the effect of ligand sterics. When functionalized with linear primary alkyl ligands that are –CH₂CH₃ or larger, the a-lattice parameter decreases with increasing chain length, and decreases even further with the bulkier secondary-butyl ligand (Figure 5.2, Table 5.5). The a-lattice parameter represents the distance between neighboring ligands on a single side of the framework. This shrinking of the lattice parameter results from partial hydrogenation of the framework, which is confirmed by the presence of Ge-H vibrational modes that appear in the FTIR as intense Ge-H stretches at around 2000 cm⁻¹ (Figure 5.3). From elemental analysis measurements of the C:H ratio, the degree of
organic functionalization of GeRₓH₁₋ₓ, ranges from x = 0.14(2)-0.69(8) (Table 5.3). Partial organic functionalization with these larger ligands is consistent with previous studies on the density of organic functionalization on Ge (111) and Si (111) surfaces. It has been reported that complete functionalization of the atop Si/Ge atoms occurs with –CH₃, –C≡CH, and –C≡CCH₃.¹⁸⁻²¹ The internuclear distance between the atop Si and Ge sites are 3.8 Å and 4.0 Å, respectively, for unreconstructed (111) surfaces, whereas these three organic ligands have van der Waals radii in the in-plane direction that are equal to or smaller than methyl, which is 2.0 Å²². However, only partial hydrogen-termination on these (111) surfaces is attained with bulkier ligands. On Si (111) surfaces, a maximum of 85% of ethyl ligands can be grafted onto the surface, due to the close non-bonding H---H interaction that occurs between hydrogen atoms on neighboring ligands.²³ Thus, it is more likely that the size of the atom or functional group at the β position, not the size of the entire ligand, is critical to determine if it can be fully grafted onto the framework or not. Comparing ligands like –CH₃, –CH₂CH₃, –CH₂CH=CH₂ and –CH₂OCH₃, though the size of the ligands increases from –CH₃ < –CH₂CH₃ < –CH₂OCH₃ < –CH₂CH=CH₂, the size of functional groups at β position increases from H in –CH₃ < O in –CH₂OCH₃ < CH in –CH₂CH=CH₂ < CH₃ in –CH₂CH₃. Since ethyl has the largest functional group at β position, it is too bulkier to fit into the germanium framework and partial hydrogenation are introduced to compensate the strain.
Figure 5. 2 XRD of GeR (R = alkyls). The starred peak is coming from the internal Ge standard and the dashed line is drawn to guide the eyes.
5.3.3 Ge(CH₃)ₓH₁₋ₓ

With larger ligands, partial hydrogenation of the germanane framework is unavoidable due to ligand size effects. Therefore to understand the influence of how homogeneously mixed ligand terminations affect the structure and properties of the framework, we synthesized Ge(CH₃)ₓH₁₋ₓ (0<ₓ<1). This was accomplished via adding different stoichiometries of HCl into the CH₃I/CH₃CN reaction mixture. The relative stoichiometry of the two ligands in the final products was determined via TGA (Figure 5.4). The loading molar ratios of CaGe₂ to CH₃I to HCl to water and the resulting x values were summarized in Table 5.8.
Figure 5.4  TGA of Ge(CH$_3$)$_x$H$_{1-x}$.

Table 5.8  Reaction condition and resulting CH$_3$ coverage (x) in Ge(CH$_3$)$_x$H$_{1-x}$.

<table>
<thead>
<tr>
<th>CaGe$_2$:H$^+$:H$_2$O:CH$_3$I</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0:10:30</td>
<td>0.95</td>
</tr>
<tr>
<td>1:0.27:10:30</td>
<td>0.73</td>
</tr>
<tr>
<td>1:0.54:10:30</td>
<td>0.47</td>
</tr>
</tbody>
</table>

The XRD patterns (Figure 5.5a) of each product show that surface functionalization occurs homogeneously throughout the sample, as there is a single reflection for the interlayer spacing in each sample, with a full width half-maximum ranging between 1° to 1.5° 2θ, for Ge(CH$_3$)$_{0.95}$H$_{0.05}$ to GeH, respectively. In contrast, when high concentrations of HCl were used as the proton source, two reflections that corresponding to the interlayer spacing were observed, due to the faster deintercalation.
kinetics of HCl. Comparing the XRD of each sample, there is a consistent and near-linear decrease in the \( a \)-lattice parameter with decreasing fractional coverage of \(-\text{CH}_3\) (Figure 5.5b). However, there is only a small decrease in the interlayer spacing from 8.6 Å to 8.4 Å for, Ge(\(\text{CH}_3\))\(_{0.95}\text{H}_{0.05}\) to Ge(\(\text{CH}_3\))\(_{0.4}\text{H}_{0.6}\), followed by a sharp 3 Å drop with GeH. This is consistent with previous observations on Ge\(_{1-x}\)Sn\(_x\)H\(_{1-x}\)(OH)\(_x\) graphane alloys\(^4\) that when >4% of the framework atoms are terminated with larger \(-\text{OH}\) ligands, the interlayer spacing is dictated by the interactions between the \(-\text{OH}\) ligands on neighboring layers. Additionally, both the energy of the E\(_2\) Raman mode, and the absorption onset decreases pseudolinearly with increasing % \(-\text{H}\), albeit with some bowing (Figure 5.6). Together this clearly demonstrates that the relative ratio of different surface functional groups on a 2D framework will influence the lattice constant, the vibrational and electronic properties, in a fashion analogous to Vegard’s Law for binary alloys of semiconductors.
Figure 5. XRD of Ge(CH₃)ₓH₁₋ₓ. In (a), the starred peak is coming from an internal Ge standard and the dashed line is drawn to guide the eyes. In (b), the a-lattice parameter (blue) is calculated from (012) reflection assuming a 6R unit cell while the interlayer spacing (red) is calculated from the first reflection in (a).
Figure 5.6 Raman and DRA of Ge(CH₃)ₓH₁₋ₓ. The dash line in (a) is drawn to guide the eyes while those in (c) highlights the absorption onset energy at the crossing points.

5.3.4 Ligand Effect on Electronic Structure

The identity of the ligand and the percent of functionalization both significantly influence the electronic and vibrational properties. First, to elucidate how ligand identity affects the properties, we compare the four germanane lattices that have nearly uniform ligand termination (–H, –CH₃, –CH₂OCH₃, and –CH₂CH=CH₂). According to numerous
theoretical simulations on group IV graphane analogs, such as the silicane derivatives,\textsuperscript{24} the Si-Si bond length is the most significant structural feature of the framework in tuning the band gap, with the band gap inversely proportional to bond length. Consequently both the ligand size and the ligand electronegativity can change the bond length and band gap. Larger ligands are expected to strain the Ge-framework in a tensile fashion, thereby providing a lower band gap. Ligands with greater electronegativity are expected and have been calculated to withdraw electron density out of the framework and lower the band gap.\textsuperscript{6, 9} The size of these four ligands decreases from –CH\textsubscript{2}CH=CH\textsubscript{2} > –CH\textsubscript{2}OCH\textsubscript{3} > –CH\textsubscript{3} > –H (Figure 5.7a). The ligand electronegativity can be estimated by the field/inductive component (F) of the Hammett constants. Going from greater to smaller ligand electronegativity, the Hammett constant decreases from –CH\textsubscript{2}OCH\textsubscript{3} > –H > –CH\textsubscript{3} > –CH\textsubscript{2}CH=CH\textsubscript{2} (Figure 5.7b). The band gap of the germanane lattice functionalized with these four ligands was determined using the absorption onset (Figure 5.7c). The absorption onset increases from GeCH\textsubscript{2}OCH\textsubscript{3} (1.45 eV) < GeCH\textsubscript{2}CH=CH\textsubscript{2} (1.55 eV) < GeH (1.57 eV) < GeCH\textsubscript{3} (1.66 eV). The trend of band gap with different ligands is consistent with the trend of the E\textsubscript{2} Raman vibrational mode, which confirms previous calculations that band gap is inversely proportional to Ge-Ge bond length. This observed band gap value increases with decreasing ligand electronegativity, with the exception of GeCH\textsubscript{2}CH=CH\textsubscript{2}. The allyl substituent is the most sterically bulky ligand of these four, and consequently strains the lattice with complete termination, resulting in a lower band gap than GeH. It is clear that neither the size nor the electronegativity of the ligand alone determines the band gap of the functionalized germanane framework.
Figure 5. 7 Ligand effect on band gap. (a) Relative size of the four ligands decreasing from left to right. (b) Relative electronegativity of the four ligands decreasing from left to right. (c) DRA of the GeR terminated with these four ligands increasing from GeCH₂OCH₃ (organe) to GeCH₂CH=CH₂ (olive) to GeH (blue) to GeCH₃ (red).
This influence of ligand identity and band gap holds to be true even for ligand chemistries that produce partially functionalized germanane lattices. The $E_2$ Raman mode energy versus the band gap determined via absorption onset of 10 different ligand functionalized germanane frameworks are plotted in Figure 5.8. Again, the band gap increases proportionally with the $E_2$ Raman shift, further confirming the relationship between Ge-Ge bond length and band gap. Generally, alkyl-functionalized germanane lattices have band gap energies that are larger than GeH, due to the electron-donating nature of these ligands. However, GeCH$_3$ has the highest energy band gap and $E_2$ Raman mode among these alkyl ligands, as partial hydrogen functionalization limits the electron-donating influence of the ligand. With electron-withdrawing ligands such as -CH$_2$I, and –CH$_2$OCH$_3$, the band gap of the functionalized germanane lattice is lower than GeH. Ligands that have low coverage densities (Ge$_{x}$H$_{1-x}$; x<0.3) typically have band gaps that are relatively close to GeH. Overall, the band gap of germanane can change by 15% from 1.45 eV in GeCH$_2$OCH$_3$ to 1.66 eV in GeCH$_3$. 
5.4 Conclusion

In conclusion, through the synthesis and characterization of germanane frameworks functionalized with a large array of ligands, we have shown how to rationally tune the electronic structure of a 2D material via the chemical identity of a covalently bound ligand. Generally, ligands that are more electron-withdrawing and have greater steric bulk will expand the Ge-Ge framework and lower the band gap, with complete ligand coverage. When functionalized with mixtures of different ligands, the band gaps and Raman shifts are dictated by the relative stoichiometry of both ligands, akin to Vegard’s law for solid solutions. We thus have provided important, systematic guidelines for the rational tuning of electronic structure of single-atom thick layered materials via ligand chemistry, which should be applicable to different families of functionalizable 2D
materials including the transition metal dichalcogenide and MXene lattices. As the multitude of exciting predictions of topological quantum spin Hall effects in the group IV graphane analogues require either appreciable tensile strain or strongly electronegative ligands to achieve band inversion, this work establishes the experimental limits to which the Ge-Ge bond lengths can be strained via surface chemistry. While the band gap decrease with the ligands shown here may not be large enough to enable experimental realization of quantum spin Hall state in germanane, the expanded tin lattice may be able to better accommodate ligands. The ability to covalently tune the band gap of germanane may prove especially useful for investigating additional phenomena, for example, the creation of lateral heterostructures by patterning multiple kinds of surface chemical groups on a single atomic sheet, or for studying excitonic behavior. Similar to how strain is used to enhance the mobility of SiGe channels in modern transistors, or how “chemical pressure” – the substitution of ions in a solid-state lattice with similar charge but different sizes – is used to optimize correlated electronic behavior such as superconductivity or charge density waves, we show that surface functionalization chemistry is a powerful approach for manipulating the electronic structure of atomically thin 2D materials.

5.5 References for Chapter 5


Chapter 6: Conclusion and Outlook

We have introduced a new family of two-dimensional (2D) materials, group IV graphane analogues. These germanium graphane analogues are real materials that can be synthesized as robust single crystals in gram-scale quantities and exfoliated into single layers. The structure, optical properties, air and thermal stability of these materials have been extensively characterized. Furthermore, the methylation method has been successfully extended to graft various organic ligands onto germanane. Through comparing the structures and properties of germananes terminated with 10 different ligands, a systematical understanding has been established on how and to what extend can the electronic structure of germanane be tailored via surface functionalization, providing a guideline to manipulate the electronic structure of 2D materials.

In principle, this novel functionalization method can be further applied to produce other group IV, silicon and tin, graphane analogues. The silicon graphane analogue is predicted to have a high mobility with sizable band gap and can be seamless integrated into the current semiconductor industry. The tin graphane analogue is particularly interesting because it is predicted to be a topological insulator when functionalized with specific ligands. Furthermore, the creation of lateral heterostructures by patterning
multiple kinds of surface chemical group on a single atomic sheet could pave the avenue to study additional phenomena.

Compared with all other 2D van der Waals solids, these group IV graphane analogues offer the capability for covalent surface termination, providing a versatile handle for tailoring the structure, stability, and electronic properties in single-atom-thick materials. Such exquisite control over the material properties makes these systems attractive candidates for a multitude of applications such as sensing, optoelectronics, and thermoelectrics and also offers the potential for new physical phenomena such as the quantum spin Hall effect. Overall, this new class of 2D materials is posed to have a great impact not only in the traditional sectors of nanoscience but also in opening up a new research paradigm in covalently controlled properties by design.
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**Chapter 2**


Chapter 3


Chapter 4


### Chapter 5


