Electronic Properties of Methyl-Terminated Germanane and Hydrogen-terminated Germanane

THESIS

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By

Xiao Yang

Graduate Program in Electrical and Computer Engineering

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Master's Examination Committee:

Professor Leonard Brillson “Advisor”

Professor Wu Lu
Abstract

Two-dimensional (2D) materials have attracted much attention in the last decade. The discovery of graphene has shown that such single-atom-layer sheets exfoliated from crystalline are fundamentally different from their parent materials. Since almost all atoms are exposed to the surface, the covalent surface termination can be used as a powerful tool to tune materials properties. Via the topotactic deintercalation of CaGe$_2$ with HCl and CH$_3$I, methyl-terminated Germanane (GeH) and hydrogen-terminated Germanane (GeCH$_3$) are synthesized. As two promising candidates to future optoelectronic and sensing applications, the physical and chemical properties of GeH and GeCH$_3$ need to be explored.

The result presented here used a complement of atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), surface photovoltage spectroscopy (SPS), cathodoluminescence spectroscopy (CLS) and photoluminescence (PL) to characterize the band gap and defect states in hydrogen and methyl-terminated germanane. The results can provide guidance to fabricate them and control defects in them.
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# Table of Contents

**Abstract** .................................................................................................................................................. ii

**Acknowledgments** ................................................................................................................................. iii

**Vita** ........................................................................................................................................................ iv

**List of Figures** ....................................................................................................................................... vi

**Chapter.1: Motivation and Introduction** ................................................................................................. 1

**Chapter.2: Measurement techniques** ....................................................................................................... 5

1. Atomic Force Microscopy (AFM) ............................................................................................................. 5
2. Kelvin Probe Force Microscopy (KPFM) .................................................................................................. 6
3. Surface Photovoltage Spectroscopy (SPS) ............................................................................................ 9
4. Photovoltage Transient (TSPS) ............................................................................................................. 11
5. X-ray Photoemission Spectroscopy (XPS) ............................................................................................ 13
6. Depth Resolved Cathodoluminescence Spectroscopy ......................................................................... 15

**Chapter.3: Result and discussion** ......................................................................................................... 17

1. Chemical bonding and elements analysis of GeCH$_3$ and GeH ......................................................... 17
2. DRCLS and SPS results of GeCH$_3$ and GeH .................................................................................... 24
3. Discussion on n-type/p-type .................................................................................................................. 34
4. PL of GeH and GeCH$_3$ ....................................................................................................................... 37

**Chapter.4: Conclusion and future work** ................................................................................................. 40

**References:** .......................................................................................................................................... 41
List of Figures

Fig. 1 (a) Scheme of topotactic deintercalation of CaGe$_2$ into GeH (b,c) Optical images. ............. 3

Fig. 2 Schematic of AFM in non-contact mode. ................................................................. 6

Fig. 3 Electronic energy level of the sample and tip in three cases (a) tip and sample are separated without electrical contact (b) tip and sample are in electrical contact (c) an external bias Vdc is applied to nullify the CPD. ................................................................. 7

Fig. 4 Schematic diagram of AM-KPFM. Lower part of the diagram is an AFM in non-contact mode and upper part is the AM mode KPFM consist of Lock-in Amplifier and feedback circuit. .............................................................................................................. 8

Fig. 5 Surface photovoltage in an n-type semiconductor (a) surface state depopulation (b) surface state population .................................................................................................................. 10

Fig. 6 Schematic of the nanoscale SPS with monochromatized light source position at KPFM cantilever............................................................................................................................. 11

Fig. 7 An example of surface photovoltage transient measurement and the parameter extracted for defect density calculation. ............................................................................................................. 13

Fig. 8 Schematic of XPS with an electron energy analyzer. .......................................................... 14

Fig. 9 Schematic of CLS measurement, with each component illustrated. ................................. 16
Fig. 10. XPS spectra of GeH(synthesis) on (a)Ge3d, (b) C1s and (c) O1s: the Ge3d peak has two peak indicating two types of bonding. ................................................................. 18

Fig. 11 XPS spectra of GeH(MBE) before cleavage on (a)Ge3d, (b) C1s and (c) O1s.............. 19

Fig. 12 XPS spectra of GeH(MBE) after cleavage on (a)Ge3d, (b) C1s and (c) O1s. .............. 19

Fig. 13 XPS spectra of GeCH₃ on (a)O1s, (b) C1s and (c) Ge3d. ........................................ 20

Fig. 14 Glove bag transfer mechanism ............................................................................ 21

Fig. 15 XPS Survey Spectra at 3 spots on GeCH₃.............................................................. 21

Fig. 16 XPS of O1s core levels at 3 spots on GeCH₃......................................................... 23

Fig. 17 (a) Core levels of Ge 3d on CaGe₂ XPS before (black) and after exposure (b)
Gaussian fit of the core levels of Ge 3d on CaGe₂ ......................................................... 24

Fig. 18 Two-dimensional CASINO simulation of Ge with the Bohr-Bethe range Rₜ of each
probe energy Eₜ noted........................................................................................................ 25

Fig. 19 (a) DRCLS of Ge and (b) band structure of Ge featuring all peaks in DRCLS spectra .... 26

Fig. 20 DRCLS of GeH in CCD range showing the bandgap of both GeH and GeO₂. ............ 26

Fig. 21 Comparison of Eₜ = 4.5 keV DRCL spectra for: (a) Ge(CH₃)₀₆Hₐ₄; (b) GeH; and (c)
GeCH₃ All three panels show IR (blue) and visible (black) spectra. ................................... 28

Fig. 22 DRCLS and SPS transition (left) compared with DFT calculation (right). .................. 29

Fig. 23 (a)AFM image of GeCH₃ sample and (b) optical microscopy of GeCH₃ surface........ 30

Fig. 24. N-type SPS spectrum of post cleaved GeCH₃...................................................... 30

Fig. 25 N-type GeCH₃ defect states with a) Photoinduced depopulation at 0.9 eV from
trap state to the conduction band  b) Photoinduced population at 1.3 eV from trap state
to the valence band (VB) ................................................................................................. 32
Fig. 26 Transient SPS measurement at 1.2 eV on GeCH$_3$..............................................................33

Fig. 30 Room temperature (300 K) photoluminescence of GeCH$_3$ .............................................38

Fig. 31 Low temperature (20k) Photoluminescence of GeCH$_3$......................................................39
Chapter 1: Motivation and Introduction

Recent studies on two dimensional (2D) van der Waals materials such as graphene and MoS$_2$ have shown a great potential to create a variety of electronic, optoelectronic and sensing applications when exfoliated into single layer.$^{1,2,3}$ Numerous studies have been developed to understand the unique properties of single-atom layer materials. Graphene, as a monolayer variant of graphite, has a linear dispersion at the K-point and massless Dirac fermions, which leads to electron mobility as high as 200,000 cm$^2$V$^{-1}$s$^{-1}$. Nevertheless, pristine graphene has no bandgap, which limits its ability to integrate into current semiconductor industry. Similar to graphene, significant changes are expected to three dimensional semiconductors such as Si and Ge when converted to their 2D analogues.$^4$ Group IV elements, unlike graphite, have larger atomic size, which increase their bond distance, making them more likely to bond with another ligand rather than its neighbor.$^5$ Furthermore, these 2D materials can have direct bandgaps, essential for the performance in photovoltaic and optoelectronic applications. Through surface functionalization chemistries, we can also modify the ligand to tune the electronic structure without disrupting the relevant electronic states. Herein, we will focus on hydrogen-terminated germanane (GeH) and methyl-terminated germanane.
(GeCH₃), both of which are synthesized by the deintercalation of CaGe₂. By varying the ligand’s size and electronegativity, the Ge-Ge bond length will vary. More electron withdrawing ligands will lengthen the Ge-Ge bond length, lowering the band gap. Compare with GeH that has a bandgap of 1.59 eV, the bandgap of GeCH₃ is 0.1 eV bigger, which is 1.69 eV. Additionally, GeCH₃ has improved thermal stability at 250°C compared to 75°C of GeH. The photoluminescence quantum yield of GeCH₃ is on the same order of magnitude as other single-layer metal chalcogenides, but doesn’t need to be exfoliated into single layer to observe such band edge emission, making it intriguing in building future optoelectronic devices.

The synthesis processes of GeCH₃ and GeH are similar, involving deintercalation of β-CaGe₂. β-CaGe₂ flakes are synthesized by sealing stoichiometric ratios of Ca and Ge in a tube, annealing to 950 to 1050 °C for 18 hours, and cooling over a period of 10 days. To get GeH flakes, these CaGe₂ flakes are treated with HCl in an oven, running at -40°C for around a week. GeCH₃, the covalently modified GeH is obtained through deintercalation in CH₃I/H₂O solvent. The CaGe₂ crystals are loaded into an extraction thimble, and fully immersed in CH₃I at room temperature for a week. Then the reaction product is rinsed in HCl and isopropanol to remove the residual CaGe₂. See Figure 1. Another method is to grow CaGe₂ films using molecular beam epitaxy (MBE) in an ultrahigh vacuum chamber, where Ge and Ca are evaporated from thermal diffusion cell and CaGe₂ thin films are formed on undoped Ge (111) wafer. Reflection high-energy electron diffraction (RHEED) is used to monitor the surface in growth and annealing
process.\textsuperscript{6} Followed by chemical processing in solution to convert into GeCH\textsubscript{3} and GeH. the film is then transferred to an insulating substrate. The thickness of the GeH is reported to be thicker than the exfoliated sample. Uniform ligand coverage can be achieved and partially oxidized termination is removed through chemical treatment. X-ray diffraction (XRD) scans has shown that the bulk structural properties are maintained as the exfoliated one.\textsuperscript{7,8}

\textit{Fig. 1 (a) Scheme of topotactic deintercalation of CaGe\textsubscript{2} into GeH (b,c) Optical images.}\textsuperscript{5}
Defects in 2D materials can create localized states that limit the mobility and change the optical properties of the materials. As observed in MoS$_2$ and other materials, deep level defects in the bandgap introduce charge trapping and scattering that limits the mobility. Comparison between optical measurement and calculated electronic structure can provide information on specific defect levels and further control these defect and optimize the performance of these 2D materials in future applications.
Chapter 2: Measurement Techniques

1. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a powerful technique to measure the sample surface topology with high resolution. By using a micro-machined cantilever with a sharp tip to measure the attractive or repulsive force, AFM measures sample topology. When the distance between tip and sample is small, the repulsive force is dominating. Typical contact mode AFM utilizes this force to measure surface topology. When the distance is larger, the attractive Van der Waals force becomes dominant. This is the region where non-contact mode AFM operates. The deflection of the cantilever is measured by an array of position-sensitive photodiodes (PSPD) through the reflection of the laser beam. See Figure 2. A feedback system controls the vertical movement of the scanner as the cantilever scan through the sample surface. The lock-in amplifier detects the change of the amplitude and phase of the cantilever when it is mechanically vibrating near its resonant frequency, which is around 100 kHz to 400 kHz. The feedback loop compensates for the changes in tip-sample distance by controlling the Z scanner.

The AFM/KPFM system used in our lab and this report is the Park Systems XE-70 with enhanced Electrostatic Force Microscopy (EFM-KPFM). To prevent noise
contamination, the AFM system site inside an acoustic enclosure with the microscope sitting upon desktop active vibration isolation table.

![Fig. 2 Schematic of AFM in non-contact mode.](image)

2. **Kelvin Probe Force Microscopy (KPFM)**

To measure the surface voltage, which is the result of work function difference, a Kelvin probe is used. Fig.3 shows the schematic of a Kelvin Probe Force Microscopy (KPFM). The basic concept of measuring contact potential difference (CPD) between the sample surface and the tip are through DC and AC bias. AC voltage generates oscillating electrical forces between the AFM tip and sample surface, and DC voltage nullifies the oscillating electrical forces. A continuous mapping of surface contact potential can be generated.
Fig. 3 Electronic energy level of the sample and tip in three cases (a) tip and sample are separated without electrical contact (b) tip and sample are in electrical contact (c) an external bias Vdc is applied to nullify the CPD. 

As shown in Fig. 3 a) depicts the energy levels of the tip and sample surface when they are not electrically connected. b) As the two are connected, their Fermi levels align and vacuum level are no longer the same, which create the contact potential difference between the two. In the last, the contact potential difference is nullified through an external DC bias. We can find the work function of the sample by measuring this DC bias voltage with a tip of known work function. In amplitude modulation mode KPFM (AM-KPFM). Electrostatic force is directly detected by the oscillation of the cantilever. The force can be expressed as: 

\[ F = -\frac{\partial C}{\partial \phi} (V_{dc} - \Delta V) V_{ac} \sin(\omega t) \] 

(1)
where $V_{dc}$ is the DC bias, $V_{ac}$ is the applied AV bias, $C$ is the capacitance of the tip-sample system, $\omega$ is the frequency of the AC signal and $\Delta V$ is the contact potential difference. The amplitude of this force is zero when CPD is equal to the applied DC bias voltage.

Two methods can be applied in amplitude-modulation KPFM (AM-KPFM). One is a dual pass process where one scan is used to generate topology while the other is the

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*Fig. 4 Schematic diagram of AM-KPFM. Lower part of the diagram is an AFM in non-contact mode and upper part is the AM mode KPFM consist of Lock-in Amplifier and feedback circuit.*

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8
KPFM measurement. The other mode is called “Dual Frequency mode” with one frequency $\omega$ applied to the tip or sample to null the potential difference between sample and tip, and another signal at cantilever resonance frequency $\omega_0$ to scan the surface for topographic information. One frequency must be much higher than the other to avoid crosstalk. Fig. 4 shows the process of KPFM measurement. An advantage of the “Dual Frequency mode” is that it will image both topography and relative work function difference at the same time, making it possible to correlate the work function with specific topological structure on nanoscale.

3. Surface Photovoltage Spectroscopy (SPS)

Surface photovoltage spectroscopy (SPS) is applied to measure the potential of the sample surface as a function of incident photon energy. Based on KPFM, SPS measure the surface potential change with nanometer scale resolution as a function of incident photon energy. The basic processes involved in SPS are shown in Fig. 5. Two types of photovoltaic effects are shown: (a) a decrease of the surface barrier due to depopulation of the surface state and (b) an increase of the surface barrier due to population of the surface state. For the n-type semiconductors with the incident light energy $h\nu > E_c - E_t$, electron in the traps states raised in energy from the localized trap states to the conduction band. The newly promoted electron from the trap states will be forced to move to the bulk of the material due to the band bending electric field.\textsuperscript{12} The photostimulated depopulation reduces the number of electrons trapped at the surface,
thus reducing the n-type band banding at surface and increasing the CPD which can be measured by KPFM. This phenomenon can be observed as an upward turn in the spectra.

In the second case where the trap state locates at $E_t$ above the valence band. With the incident light energy $hv > E_t - E_v$, an electron will be excited from the valence band to populate the defect state, adding an electron that is now trapped at the surface, which will increase the surface negative charge and therefore the surface band bending. A downward turn in the CPD spectra will be observed in this case. Fig.6 shows the schematic of a nanoscale SPS. In addition to the AFM-KPFM set up, the monochromator will scan the wavelength of the incident light from the light source. The change on the potential difference will then be recorded by the lock-in amplifier, which measures the feedback voltage required to null out the voltage difference between semiconductor surface and AFM tip.

![Graph showing band structures and photovoltage](image)

Fig. 5 Surface photovoltage in an n-type semiconductor (a) surface state depopulation (b) surface state population.
Fig. 6 Schematic of the nanoscale SPS with monochromatized light source position at KPFM cantilever.\textsuperscript{14}

4. Photovoltage Transient (TSPS)

SPS can also provide information of surface state parameter such as density and fractional occupancy in a transient method. In order to maintain the charge neutrality between the bulk and the surface, the change in surface charge must be equal to the change in the electrical charge in space charge region.\textsuperscript{13}

\[-Q_{SS} = Q_{sc} = (2\varepsilon k_B T N_b)^{\frac{1}{2}} (V_s)^{\frac{1}{2}}\]  \hfill (2)

where $\varepsilon$ is dielectric permittivity of the bulk, $N_b$ is the free electron density in the bulk $T$ is the temperature in K and $V_s$ is the Schottky-type barrier height in dimensionless units (kT). One can obtain the following equation of electron variation $\delta n_t$ trapped at $E_t$ as a function of changes in barrier height:

\[
\delta n_t = -\frac{(2\varepsilon k_B T N_b)^{\frac{1}{2}} \delta V_s}{2q(V_s)^{\frac{1}{2}}} \]  \hfill (3)
The rate of change in the density of the occupied state can be expressed as

\[
\frac{dn_t}{dt} = -K_{ph}^d n_t I + K_n n_s p_t - K_n n_s n_1
\]  

(4)

where \( K_{ph}^d \) is the capture cross section of the surface states for photons, \( I \) is the light intensity, \( K_n \) is the capture cross sections of the surface state for electron, \( n_s \) is the density of free elections at the surface. \( p_t \) and \( n_t \) are the density of captured electron and holes at the surface states and \( n_1 \) is the emission constant. At \( t = 0 \), where the sum of second term and the third term is equal to zero due to thermal equilibrium.

\[
\frac{dn_t}{dt} = -K_{ph}^d n_t I
\]  

(5)

Combined with equation (3),

\[
\frac{dV_s}{dt} = \frac{-K_{ph}^d n_t^2 q(V_s) \frac{1}{2}}{(2\pi k_B T N_b)^{\frac{1}{2}}} I
\]  

(6)

A typical photovoltage transient schematic is shown as Fig. 7. \( \delta V_s^1 \) is the surface potential difference before and after light on. \( V_s^1 \) is the initial surface potential without light in dimensionless units. The value of \( K_{ph}^d \) can be obtained as :

\[
K_{ph}^d = (V_s^0 + \dot{V}_s^1) / (I \delta V_s^1)
\]  

(7)

Since the value of \( K_{ph}^d \) is determined with photon intensity and the quantities from the photovoltage transient, the surface density state can be obtained by substituting it into equation (5):

\[
n_t^0 = \frac{\delta V_s (2\pi k_B T N_b)^{\frac{1}{2}}}{2q(V_s)^{\frac{1}{2}}(1+\dot{V}_s^1/\dot{V}_s^0)}
\]  

(8)
Fig. 7 An example of surface photovoltage transient measurement and the parameter extracted for defect density calculation.

5. X-ray Photoemission Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) provides quantitative analysis of materials which include but are not limited to: elemental composition of the surface (0-10nm), chemical state of each element on the surface and thickness of one/more thin layers of different materials within the top surface. In XPS operation, photoelectrons are emitted as a consequence of Al Kα X-ray excitation which interacts with atoms in the surface region of the sample by photoelectric effect under an ultra-high vacuum condition. The kinetic energy of emitted electron can be measured by a hemispherical analyzer as:

\[ KE = hv - BE - \phi_s \]  

(9)
where $KE$ is the kinetic energy of the emitted electron, $hv$ is the photon energy from the X-ray excitation and $BE$ is binding energy of the electron and $\phi_s$ is the work function dependent on both the spectrometer and the material. Fig. 8 shows the schematic of XPS. The MBE Oxide Laboratory houses the 5000 VersaProbe XPS system. Monochromatic X-ray is generated by scanning on an Al anode with electron beam energy of 1486.6 eV (Al $K\alpha$). The resolution of our hemispherical analyzer is \(^\sim\)0.046 eV.

Fig. 8 Schematic of XPS with an electron energy analyzer.\(^{16}\)
6. Depth Resolved Cathodoluminescence Spectroscopy

Similar to photoluminescence spectroscopy (PLS), Cathodoluminescence Spectroscopy (CLS) create electron-hole pairs, subsequent recombination and optical emission which includes conduction band to valence band transition, band to gap states transition, gap states to band transition or gap states to gap states transition.\textsuperscript{17} However, instead of producing optical transition with photon, it utilizes electrons. The main advantage of CLS over PLS is that in CLS, the electron beam can probe from tens of nanometers up to several micrometers below the surface by varying the probing electron energy. Also, it has a beam energy that has a much higher free carrier generation rate, making it suitable for various materials including indirect bandgap material. Using electron beam energies between 0.2 kV to 5.0 kV, Depth resolved cathodoluminescence spectroscopy (DRCLS) allows us to measure these 2D materials on a nanometer scale. In particular, we can combine the measured result with Monte Carlo simulation such as CASINO to associate the electron beam energy with particular depths in the sample.\textsuperscript{18} Fig.9 shows the schematic of DRCLS.
CASINO simulates large quantities of electrons trajectory to predict excitation depth and volumes in different electron beam energies settings. The X-ray emission, backscattered electrons and lateral beam widening could also be predicted by this program. The program can also be used to simulate through multiple layers with different densities and atomic weights. Experimental results have shown that CASINO simulation can provide precise depth of peak excitation values for CLS.
Chapter 3: Result and discussion

1. Chemical bonding and elements analysis of GeCH$_3$ and GeH

XPS is utilized to identify the chemical composition, bonding and surface contamination of GeH and GeCH$_3$ sample. Elements found on GeH (synthesis method) surface includes Ge, O, C, Cl, Ca. The atomic percentage of Ge, C and O on GeH sample is 62.7%, 23.0% and 14.2% respectively. Fig.10 shows the XPS core levels of Ge, C and O. C1s core levels has two peaks at 32 eV and 29 eV. The 29 eV peak is from the intrinsic Ge-Ge bonding. A shift in the Ge3d peak energy is expected because oxygen is less electronegative than the germanium. Because oxygen, carbon oxide and other gas could be absorbed on the sample surface, such impurities will be released when samples are heated by X-ray exposure. To obtain a more accurate estimate of the atomic concentration, a clean sample with less oxygen is needed. MBE grown GeH is also scanned by XPS. The initial atomic percentage of Ge, O, C on GeH sample is 52.9%, 20.9% and 26.2%. In Fig.11, The broadening of the Ge3d peak indicates the presence of oxide and 529.8 eV peak in the O1s spectrum is the evidence of a metal oxide. To remove the oxygen contamination on the top of the surface, we used Scotch tape to peel off the top layer of MBE grown GeH sample. The atomic concentration of Ge:O:C becomes 59.0%:
8%: 32%. The percentage of oxygen drops from 20.9% to 8%. Fig. 12 shows the change: The O1s peak in Fig. 12 (c) becomes noisy indicating a decrease in oxygen content and Ge3d peak does not seem to be broad at the base indicating a decrease in GeO or GeO$_2$. However, an extra peak appears on C1s peak, which is possibly caused by the residue of the Scotch tape.

Fig. 10. XPS spectra of GeH(synthesis) on (a)Ge3d, (b) C1s and (c) O1s: the Ge3d peak has two peak indicating two types of bonding.
Fig. 11 XPS spectra of GeH(MBE) before cleavage on (a) Ge3d, (b) C1s and (c) O1s.

Fig. 12 XPS spectra of GeH(MBE) after cleavage on (a) Ge3d, (b) C1s and (c) O1s.
XPS on GeCH₃ samples that are grown by two methods are also performed. Fig. 13 shows the core level difference of GeCH₃ made by MBE growth and synthesis. Air contamination on the sample surface are in the same amount. However, this synthesis method has a much higher carbon concentration of ~ 60% more than the MBE growth method as shown in Fig. 13. Similar to the GeH flake made by MBE growth, C1s peak on MBE grown GeCH₃ has two peaks as well, which could be the result of C-O bonding. The broadening of the Ge3d peak also indicates the presence of Ge-O bonding. In summary, we compare two different approaches to topochemically prepare GeCH₃/GeH through XPS core level analysis. The synthesis method product always has a lower percentage of oxygen contamination, although cleaving the sample with Scotch tape can remove part of the contamination. To fully study the sample structure and bonding between elements, it’s crucial to transfer and study the sample without air contamination since the potential utility of GeCH₃ and GeH for any functional device strongly hinges on their air stability.
Fig. 14 Glove bag transfer mechanism

Fig. 15 XPS Survey Spectra at 3 spots on GeCH$_3$
We developed an air-free method to transfer sample between the sealed glove box and the XPS intro chamber. As shown in Fig. 14 the process of transferring sample involved a glove bag and a container. The sealed container is transferred from the glove box where the germanane synthesized to the XPS intro chamber. Positive pressure of nitrogen will displace the oxygen from the sample surface to create an air-free environment. Fig. 15 shows the XPS survey spectra at 3 spots on GeCH$_3$. A closer look at O1s peak is shown as Fig. 16. At spot 3, on the edge of the sample O1s peak is the highest. The intensity of O1s drops between the center of the sample and the edge at spot 2. At the center of the sample, spot 1, there is no oxygen. The atomic concentration ratio between Ge:C is very close to 1 considering the attenuation due to layered structure, which suggests that we are on a spot that only has GeCH$_3$ without any oxygen contamination. This transfer mechanism proved that it is possible to transfer sample without air exposure. It can be used in further experiment such as DRCLS to investigate the true nature of the sample without air exposure.
To observe how the air exposure changes the surface chemical bonding, we also did XPS on CaGe$_2$ and exposed it to air for 2 weeks. After 2 weeks of exposure in air, the oxygen content in the sample increased from 40% to 60% and two new peaks are observed on the Ge3d peak, which provide us a rough gauge of the rate of oxidization. It also helps us to identified the peak on Ge core levels. As shown in Fig. 17, the 30 eV/29.4 eV peak corresponds to Ge-Ge bonding, the 25 eV peak corresponds to Ge-Ca bonding and the 32.9 eV peak corresponds to Ge-O bonding. This energy difference of 3 eV agrees with the previous result of energy difference between GeO$_2$ and GeCH$_3$. 

Fig. 16 XPS of O1s core levels at 3 spots on GeCH$_3$
Fig. 17 (a) Core levels of Ge 3d on CaGe$_2$ XPS before (black) and after exposure (b)

Gaussian fit of the core levels of Ge 3d on CaGe$_2$.

2. DRCLS and SPS results of GeCH$_3$ and GeH

The optical properties of GeH and GeCH$_3$ are investigated by DRCLS and SPS. We first studied the CLS of Ge substrate. Fig.18 shows the two-dimensional CASINO simulation of the Ge substrate. It can be seen that with high energy electron beam, we can probe to up to 74 nm deep beneath the surface. This could reduce the effect of interface defects generated from surface oxidization.
**Fig. 18 Two-dimensional CASINO simulation of Ge with the Bohr-Bethe range $R_B$ of each probe energy $E_B$ noted.**

Fig. 19 shows DRCL spectra with incident beam energy range from 1 keV to 5 keV in the visible range at room temperature as well as the band structure of the Ge. Red arrows indicated the transition we observed in DRCLS. The CLS peak agree with the known energies of interband transition, which are $L_{6c} \rightarrow L_{4,5v}, \Gamma_{8c} \rightarrow \Gamma_{7v}, X_{5c} \rightarrow X_{5v}$ and $L_{6c} \rightarrow L_{4,5v}$. 3.0 eV peak is the band gap energy of GeO$_2$ \cite{19}, which are also observed in the GeH sample. Based on these information, we can eliminate the background signal from Ge substrate in further DRCLS experiments.
Fig. 19 (a) DRCLS of Ge substrate and (b) band structure of Ge featuring all peaks in DRCLS spectra\textsuperscript{19}

Fig. 20 DRCLS of GeH in CCD range showing the bandgap of both GeH and GeO$_2$. 
Fig. 20 shows DRCL spectra of GeH flake with incident beam energy range from 1 keV to 3 keV in the visible range at room temperature. The 3.0 eV peak is the band gap energy of GeO$_2$ and 1.54 eV is the direct band gap of GeH. This energy is in good agreement with diffuse reflectance absorption (DRA) measurements reported earlier for GeH flakes. A closer look on band structure to the energy range below the visible light is done by T. Asel. As shown in Fig. 21, the 0.96 eV, 0.81 eV, and 1.35 eV feature are in all three spectra of GeH, GeCH$_3$ and Ge(CH$_3$)$_{0.6}$H$_{0.4}$, which suggested that these defect states are related to the germanium scaffold instead of ligand termination. To investigate the electronic structure below visible light range, a Ge detector was installed. In fig. 21(c), the 1.02 eV defect disappears which is a result of the extended duration time of the CaGe$_2$ deintercalation. This indicates that the 1.02 eV feature is caused by the incomplete removal of CaGe$_2$ between GeCH$_3$ layers.

The band structure of GeCH$_3$ combined with experimental result obtained from DRCLS and SPS is shown as Fig. 22. First principles calculations developed from three dimensional semiconductor using density functional theory is applied to predict the location of the surface defects. The theoretical value of the mobility can also be calculated using this method, which is about 18,200 cm$^2$ V$^{-1}$ s$^{-1}$. 21
Fig. 21 Comparison of $E_0 = 4.5$ keV DRCL spectra for: (a) Ge(CH$_3$)$_{0.6}$H$_{0.4}$; (b) GeH; and (c) GeCH$_3$. All three panels show IR (blue) and visible (black) spectra.}$^{20}$
Fig. 22 DRCLS and SPS transition (left) compared with DFT calculation (right).  

Fig. 23 gives a typical AFM image of the GeCH$_3$ sample and its optical image.

Before taking AFM and KPFM data, each sample is cleaved with Scotch tape to remove any oxygen contamination. All AFM and KPFM data were taken at atmosphere and at room temperature. To aid in the conduction of the DC bias through the insulating sample, silver paste was applied on the steel disk. Before each SPS scan samples were
also illuminated with white light to excite the static charge build up by the DC bias as well as the motion of the cantilever near the surface.

Fig. 23 (a)AFM image of GeCH3 sample and (b) optical microscopy of GeCH3 surface.

Fig. 24. N-type SPS spectrum of post cleaved GeCH3.
Fig. 24 shows an SPS spectrum of GeCH$_3$ after cleavage. A significant slope change starting at 1.6 eV is the result of band-to-band transition. The onset of 1.6 eV band gap is in good agreement with the 1.56 eV emission in DRCLS measurement. And the upward band gap change identifies that this material is n-type material. Other slope changes are also noted on the plot at 0.85, 1.05, and 1.40 eV. Based on the sign of the slope change, one can identify the electronic structure of the material. The 0.85 eV transition corresponds to a state 0.85 eV below the conduction band, according to the DFT calculation, due to either a Ge vacancy or Ge divacancy bonded with H. The 1.40 eV transition matches the 1.38 eV peak from the DRCLS, correspond to a state 1.40 eV below the conduction band based on the direction of the slope change, which is 0.2 eV above the valence band. Fig. 25 shows the depopulation and population of these states and how the band bending is changed due to the defect state under particular energy. This is in good agreement with the DFT calculation of feature corresponding to a Ge vacancy with 1 H. Considering the resolution of the spectral resolution of DRCLS and SPS are 0.04 eV and 0.05 eV respectively, one can see there is a good agreement with these theory and experimental techniques.
A Transient SPS (TSPS) was performed at 1.2 eV, with incident light on from \( t_0 = 30 \) s to \( t_1 = 130 \) s, the change of the contact potential difference was recorded and analyzed to determine the density of the defect states. Incident energy at 1.2 eV exceeds the transition energy of the defect at 1.05 eV. This yields surface state densities of \( 1.5 \times 10^{10} - 4.8 \times 10^{11} \text{ cm}^{-2} \) for assumed bulk carrier densities of \( 10^{15} - 10^{18} \text{ cm}^{-3} \), respectively. See Table I, which shows the defect state concentration \( (N_t) \) calculated based on different bulk density. Fig. 26 illustrates the parameters extracted for defect state calculation with following equation:

\[
n_t^0 = \frac{\delta V_s (2\varepsilon k_B T N_p)^{\frac{1}{2}}}{2q (V_s)^2 (1 + V_s / \nu_s^0)} \tag{10}
\]

where \( n_t^0 \) is the density of electrons captured by defects, \( \delta V_s \) is the surface potential difference before and after light on, \( \varepsilon \) is the dielectric permittivity of Ge bulk, \( k_B \) is the Boltzmann constant, \( T \) is temperature in K, \( N_p \) is electron density in the bulk. \( V_s \) is the
initial surface potential without light in dimensionless units. \( \dot{V}^1_s \) is the slope of surface potential changing with light on, and \( \dot{V}^0_s \) is the slope of surface potential changing with light off.

<table>
<thead>
<tr>
<th>( N_b (\text{cm}^{-3}) )</th>
<th>( N_t (\text{cm}^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{15} )</td>
<td>( 1.51 \times 10^{10} )</td>
</tr>
<tr>
<td>( 1 \times 10^{16} )</td>
<td>( 4.77 \times 10^{10} )</td>
</tr>
<tr>
<td>( 1 \times 10^{17} )</td>
<td>( 1.51 \times 10^{11} )</td>
</tr>
<tr>
<td>( 1 \times 10^{18} )</td>
<td>( 4.77 \times 10^{11} )</td>
</tr>
</tbody>
</table>

*Table 1 Defect state concentration (\( N_t \)) calculation based on different bulk density (\( N_b \)).*

*Fig. 26 Transient SPS measurement at 1.2 eV on GeCH₃*
Fig. 27 shows the bandgap transition measured by DRCLS, SPS and predicted Kubelka-Munk function. The onset of SPS slope change, the peak of CL measurement and the Kubelka-Munk model yield the same result for band gap.

![Graph showing bandgap transition measured by different techniques](image)

*Fig. 27 Band gap of GeCH$_3$ measured by SPS (black), DRA (red) and DRCLS (blue).*

3. **Discussion on n-type/p-type**

   In contrast to the N-type band bending we observed in Fig. 24, a p-type band bending is also observed on GeCH$_3$ sample. Fig. 28 shows the major decrease in $\Delta$cpd starts at 1.65 eV, corresponding to onset of valence-to-conduction band transitions that flatten the band bending. This is the same value obtained from the n-type sample. The sign of $\Delta$cpd indicates that this materials is p-type and there is no significant variation in
feature across the cleaved surface even though the potential map in Fig. 29 shows that there exist about 200 mV difference between point 1 and point 3.

**Fig. 28** P-type SPS spectra of post cleaved $\text{GeCH}_3$ on different spots

**Fig. 29(a)** Potential mapping and (b) Topology of p-type GeCH$_3$
The change of n-type and p-type band bending could be explained by the defect as well as the defect-chemistry-related variation in the local stoichiometry.\textsuperscript{22,23} Multiple papers have suggested explanations for the conductivity change in 2-D material. For example, n-type behaviors of MoS\textsubscript{2} is observed when the stoichiometry of MoS\textsubscript{2} appears to be $\sim$1.8:1 (S/Mo) due to sulfur vacancy. For p-type MoS\textsubscript{2}, the stoichiometry is $\sim$2.3:1 (S/Mo), which is observed with lower binding energy of both Mo and S core levels.\textsuperscript{22} The origin of n-type/p-type conversion in GeCH\textsubscript{3} can be explained in a similar way. When the surface is methyl rich or germanium deficient after exfoliation, the binding energy of Ge and C core levels shift to higher energy, making the system n-type since the binding energy of the core level measured in XPS is referenced to the fermi level of the material. As shown in Fig.16, the binding energy of both Ge3d and C1s core levels shift to higher energy after exfoliation. We also observed the Ge/C ratio decrease in XPS, suggesting that n-type behavior can be correlated to area with lower germanium concentration. To further analyze the conductivity of the sample, a vacuum chamber is needed to eliminate the interference of the oxygen during measurements.

The dangling bond in GeCH\textsubscript{3} impurities might also play an important role in determining the conductivity of the GeCH\textsubscript{3} sample. Because of the localized states that arising from the oxide layer, the effective Fermi level of the system is repositioned. As showed previously, the ratio between Ge and C in XPS spectrum is not identical. The extra Ge concentration suggests that some of the methyl ligand are not fully synthesized with the germanane from CaGe\textsubscript{2}, creating some dangling bond on the surface. An oxide
layer is formed slowly as the surface potential is being measured. Such impurities can form trap states that produce a modification of electrostatic potential, which is measured by KPFM. During SPS measurement, charged traps originated from these newly-formed states can influence the depletion/accumulation of electron, which results in the change of conductivity. When oxygen absorbs onto the surface, electron charges transfer from GeCH$_3$ to O atoms, result in a positively charged donor in the surface space charge region that produce a n-type band bending in SPS. On the contrary, when hydrogen absorbs onto the surface, electron charges transfer the other way, result in a negatively charged acceptor in the surface space charge region that produce a p-type band bending in SPS. Unlike MoS$_2$, the bandgap of GeCH$_3$ is unchanged whether it’s n-type or p-type.\textsuperscript{23}

4. \textit{PL of GeH and GeCH$_3$}

Previously studies report that GeH is a direct band gap material with a band gap of 1.80 eV.\textsuperscript{24} However, we did not observe any photoluminescence from 1.5 to 3.1 eV. The lack of photoluminescence might suggest that this is an indirect band gap material. However, the lack of photoluminescence could also be caused by a large concentration of defect states or impurities or there exists unique surface or edge states on the sample. The PL of GeCH$_3$, as shown in Fig.30, is easier to observe with the naked eye. Here, we used a 200 mW HeCd as the excitation source, with the laser energy of 3.815 eV (325 nm). The cryo-stage is connected by a mechanical pump in the initial setup. We
modified the port to connect a gas source to investigate the physical absorption of the sample. Two peaks are observed on the spectrum, one at 1.78 eV and the other at 1.65 eV. This red shift is caused by the deintercalation of water vapor since the experiment is done in air. A low temperature (20k) measurement was also done using the cryo-pump. Similar to the room temperature experiment, two peaks are observed with the same energy splitting between them which is cause by the spin-orbit coupling. This agrees with the HSE06 theory.

![Graph showing energy levels and counts](image)

**Fig. 30 Room temperature (300 K) photoluminescence of GeCH₃ in air.**

Contrary to what we expect with the photoluminescence of other materials in low temperature, the band gap of the GeCH₃ is lower than the band gap measured in room temperature. This anomalous phenomenon can be explained by the physical adsorption on the surface. Further experiment done by A. Barnum has shown that water vapor can alter the measured bandgap for more than 0.1eV because the carrier density
in the surface space charge region is changed due to gas adsorption.\textsuperscript{25} As the water vapor and other gas cooled down to low temperature, they condensed inside the chamber. The full width half maximum value of the signal in low temperature experiment is also lower than the one in room temperature, making the peak sharper even though the intensity of the signal is lower by an order of magnitude. This can be explained by the decreased lattice scattering in the sample. As the temperature decreases, the lattice vibration also decreases, which makes the probability of a scattering event decrease.\textsuperscript{23}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig31}
\caption{Low temperature (20k) Photoluminescence of GeCH\textsubscript{3} in vacuum.}
\end{figure}
Chapter 4: Conclusion and future work

This study has characterized and analyzed the defect and bandgap in germanium graphane analogue namely methyl-terminated germanane(GeH) and hydrogen-terminated germanane(GeCH₃), utilizing various surface characterize technique, including DRCLS, AFM, SPS and PL. The chemical bonding of each element is carefully analyzed. We have also quantified the defect states on the GeCH₃. My SPS measurements provide very good agreement with the CLS and DFT results. They provide absolute energy level positions within the band gap of GeCH₃ which show the nature of the electronic transitions measured by CLS and calculated by DFT theory. They also provide an energy level transition associated with Ca impurities that allows us to compare our experimental results successfully with theory. Overall the combination of techniques that I have used for this work provides an effective tool for identifying point defects in GeCH₃, a representative Van der Waals solid.


11. Hao S. KPFM foundation unpublished


