STRATEGIES FOR THE ATTACHMENT OF ORGANIC FUNCTIONAL GROUPS TO SILICON SURFACES AND MEASUREMENT OF VAPOR PRESSURE OF IONIC LIQUIDS

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STRATEGIES FOR THE ATTACHMENT OF ORGANIC FUNCTIONAL GROUPS TO SILICON
SURFACES AND MEASUREMENT OF VAPOR PRESSURE OF IONIC LIQUIDS

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A candidate for the degree of doctor of philosophy,
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ABSTRACT

Surface modifications of silicon surfaces have been studied for several decades. There are several approaches for attaching organic molecules with specific functionalities to these surfaces, utilizing both the selectivity of organic molecules, and the electronic properties of silicon. In this thesis we describe two strategies for attaching a fluorophore to chemically modified Si (100) surfaces as the base of a chemical sensor. By using the first strategy, a direct –NH termination was created on silicon surface after HF etching, chlorination and ammonia treatment. In the second strategy, an alkene with protected amine termination was first connected to the silicon surface by reaction with the hydrogen covered surface. Then the –NH termination was created after a protection-removal step. Both of the resulting –NH covered surfaces underwent an amination reaction in order to attach an aryl alkyne. The Si surfaces are
characterized using X-ray Photoelectron Spectroscopy (XPS) and these results were presented and discussed.

Ionic liquids represent a relatively new group of compounds that are thermally stable with very low vapor pressures. These unique properties enable ionic liquids to be used in a variety of applications. As the family of ionic liquids keeps growing, there is a need for vapor pressure and thermodynamic data for the vast majority of ionic liquids. In this thesis, the Knudsen effusion method is used to determine the vapor pressure of several ionic liquids in the temperature range of 380 to 420K. The relationship between the structure of ionic liquids and vapor pressure was discussed based on the vapor pressure data.
Chapter 1: Introduction

1.1 Ionic Liquids

Ionic liquids are a new class of purely ionic, salt-like materials that are liquid at unusually low temperatures even at room temperature. Since their discovery\(^1\) in 1914, the unique chemical and physical properties of these materials has attracted great interest from both research and industrial communities.

1.1.1 Structure of ionic liquids

An ionic liquid consists of a cation and an anion, and most commonly used anions and cations are shown in Figure 1.1 and Figure 1.2, respectively. Generally, size\(^2\), geometry\(^3\) and charge distribution\(^4\) determines the property of an ionic liquid. In most cases, water miscibility is determined by the anion\(^5\). The amazing part of ionic liquids is that numerous ionic liquids can be made by varying the cation and anion, as well as changing the alkyl group attached to the cation and anion. Thus researchers can utilize ionic liquids made by selecting cations and anions that fit their needs.

![Anion Chart](image)

Figure 1.1 Common anions that form ionic liquids.
1.1.2 Properties of ionic liquids

The most surprising discovery of ionic liquids is most ionic liquids do not evaporate since they have very low vapor pressures\(^6\). Even though Widegren\(^7\) reported that ionic liquids have low, but detectable vapor pressure, and thus can be distilled\(^8\).
Other properties of ionic liquids include high thermal conductivity, a wide electrochemical window, strong polarity, and relative stability to heat and air.\(^9\)

### 1.1.3 Application of Ionic Liquids

Ionic liquids have been called “green solvents”, that represents its most valuable application as the substitute of traditional organic solvents. Since they have several advantages over the traditional organic solvents in environment, toxicity, volatility and solubility.

Earle\(^{10}\) reported by selecting different ionic liquid solvents, the outcomes of a given reaction differs as shown in Figure 1.3. In reactions between toluene and nitric acid, by using three different ionic liquids, the product of the reaction would be benzoic acid, nitro benzene and halogen substituted toluene. This opens a broad potentially useful application of ionic liquids which can influence the products of a reaction.

Ionic liquids are also widely used in electrochemistry due to their excellent properties including good ionic conductivity, wide electrochemical potential window, high viscosity and tunable solvent properties. They are often used as electrode interface material and as electrolytes, they also have applications in electrosynthesis and electrodeposition\(^{11}\).
Figure 1.3 An example of how different ionic liquids can influence the outcome of a reaction.
1.2 Determination of vapor pressure of ionic liquids

Since ionic liquids are known to have several applications, vapor pressure becomes important. In addition, the thermodynamic properties of IL vaporization, in particular the enthalpy of vaporization is closely linked to lattice, cohesive, and configurational energies, thus lead to a better understanding of structure, interaction and behavior of ionic liquids. A better and more complete picture of vapor pressure and thermodynamic data for ionic liquids will aid in design and execution of chemical processes.

1.2.1 Conventional methods of vapor pressure measurement

1.2.1.1 Direct measurements

Methods of vapor pressure measurement include direct measurements and indirect measurements. For direct measurements, the sample is placed in a vacuum system, and the vapor pressure is measured directly by a pressure gauge. This method is less commonly used because most ionic liquids studied have relative low vapor pressure and thus cannot be measured directly.

1.2.1.2 Knudsen Effusion

Knudsen effusion\textsuperscript{12} is an indirect method to measure vapor pressure. A sample is placed in a sample cell with a hole in the top lid. The sample cell is placed under vacuum condition, and is heated to a preset temperature. The capsule is held at constant temperature in vacuum. Assuming the sample maintains its equilibrium vapor pressure
inside the capsule, the gas phase molecules of sample leak out through the hole into vacuum over a period of time at constant temperature, and the number of molecules escaping can be determined by mass loss. A schematic of Knudsen effusion apparatus is shown in Figure 1.4.

![Figure 1.4 Schematic of Knudsen effusion apparatus. A: Knudsen cell, B: temperature control unit, C: Flange joint, D: liquid nitrogen cold trap, E: isolation valve, F: turbomolecular vacuum pump, and G: pressure gauge.](image)

The mechanism of Knudsen effusion is shown in Figure 1.5. There are two conditions which Knudsen effusion is based on, (1) the area of the hole \( A_0 \) should be
much smaller than the area of the sample cell in order not to disturb the velocity and density distribution in the gas. (2) A low pressure is necessary to keep air molecules from limiting the mean free path of the vapor molecules. A low total pressure then ensures a long mean free path.

![Figure 1.5 Mechanism of Knudsen effusion.](image)

**1.2.1.3 Torsion Effusion**

In a torsion-effusion method\textsuperscript{13}, as shown in Figure 1.6 a sample cell loaded with sample is hung in vacuum chamber by a wire often made of tungsten. At a certain temperature the sample evaporates inside the sample cell and then the gas phase molecules leak out through a hold on the side of sample cell, thus creating effusional torsion. This effusion torsion is proportional to the density of gas phase cluster leaking out of the side hole. By measuring the torsion angle using the optical device, the effusion torsion can be determined. The vapor pressure can be determined by $p=K\alpha$, where $\alpha$ is the torsion angle and $K$ is a constant which is related to the physical property
of the sample cell and the hanging wire. The value of K can be calculated by conducting a calibration trial using a standard with a known vapor pressure, such as naphthalene or mercury.

![Schematic of a torsion effusion apparatus](image)

Figure 1.6 Schematic of a torsion effusion apparatus.

1.2.1.4 **Error sources**

Errors involved in vapor pressure measurements are mostly due to two aspects, temperature stability and impurities. For some measurements, temperature is maintained in a temperature range instead of the preset temperature point.
Fluctuations in temperature will result in a change in vapor pressure, thus affecting the related parameter recorded, including mass lost or torque generated. These fluctuations all lead to an error in the determination of the vapor pressure. Impurities, especially volatile impurities affect vapor pressure measurement as well, since impurities will also evaporate and generate mass lost or torque, regardless of the method used.

1.2.2 New methods developed for ionic liquid vapor pressure measurements

The methods introduced in section 1.2.1 are proven to be reliable for vapor pressure measurement of volatile solids and liquids. As mentioned in section 1.1.2, ionic liquids have extremely low vapor pressure, making most of the conventional methods except Knudsen effusion not suitable for vapor pressure measurements of ionic liquids. In recent years, several new methods were reported specifically for determination of extremely low vapor pressure materials. These methods include thermogravimetry (TGA), quartz crystal microbalance (QCM), temperature programmed desorption (TPD) and high temperature UV spectrometry.

1.2.2.1 Thermogravimetry method (TGA)

In a thermogravimetric analysis, a sample is continuously weighed while it is placed under a constant temperature. As sample evaporates, the mass of sample decreases. According to the Langmuir equation, the rate of mass lost can be described in the following equation:
Where $P$: vapor pressure, $\alpha$: the vaporization constant, $T$: the absolute temperature, $R$: the universal gas constant, and $M$: molecular weight of the evaporating vapor.

By using the rate of mass lost data from TGA, the pressure can be determined at different temperatures. Baker$^{16}$ studied a series of imidazolium based ionic liquids using the TGA method and reported the vapor pressures and vaporization enthalpies.

### 1.2.2.2 Quartz crystal microbalance (QCM)

Verevkin$^{17}$ reported measuring vapor pressures using a quartz crystal microbalance. A schematic of the apparatus is shown in Figure 1.7. This set up is similar to a Knudsen set up as mentioned in section 1.2.1.2. The sample is placed in an open sample cell heated to preset temperature. As the sample evaporates, some of the sample will condense and deposit on the surface of quartz crystal placed just above the sample cell. The additional mass deposited on the surface of the quartz crystal will change its oscillation frequency. The deposit rate of the sample can be determined by the data collection and processing device. As QCM is a very sensitive method to detect any mass change, using QCM method enables vapor pressure determination at temperature 100 °C lower than using a TGA method.

\[
\frac{dm}{dt} = P\alpha \left( \frac{M}{2\pi RT} \right)^{1/2} 
\]
1.2.2.3 Temperature programmed desorption (TPD)

Taylor\textsuperscript{18} reported vapor pressure measurement using the temperature programmed desorption method. A thin layer of ionic liquid is placed on a silver dipstick by immersing the dipstick into an ionic liquid. The silver dipstick is placed in vacuum
chamber and its temperature is changed at a constant rate. The ionic liquids completely evaporated and the vapor was monitored by line-of-sight mass spectrometry (LOSMS) which only focused on the vapor passing by line of sight from a small patch on the dipstick surface.

1.2.2.4 High temperature UV spectrometry

Wang\textsuperscript{19} reported vapor pressure measurements by UV spectrometry. The ionic liquid sample is placed in an apparatus similar to a distillation set up where it is heated to high temperature and evaporates. The vapor of ionic liquid sample is then analyzed by a UV spectrophotometer, and the spectrum is similar to the spectrum of its aqueous solution. The absorption of the ionic liquid is plotted as a function of temperature to obtain the vapor pressure and vaporization enthalpy.

1.2.2.5 Validity of vapor pressure data of ionic liquids

An existing issue that can affect the validity of vapor pressure of ionic liquids is that some ionic liquids are not stable at elevated temperatures (473K and beyond). Therefore, the vapor pressure measured at higher temperatures may be inaccurate. Furthermore, a number of vapor pressure data is obtained by extrapolation of the known value beyond certain temperature range, this can also lead to inaccurate data. In this thesis, all the vapor pressure measurements were conducted at a temperature range between 373K and 423K.
1.3 Semiconductors, silicon and modification of silicon

Semiconductors are materials where its conductivity falls between a conductor and an insulator. Current flow in a semiconductor is produced by the movement of free electrons or holes. The conductivity of semiconductors can be controlled by adding impurity atoms into the material in a process known as “doping”. Doping a semiconductor changes the abundance of free electrons and holes. A doped semiconductor containing mostly free holes is called "p-type" and when it contains mostly free electrons it is known as "n-type". Because of this unique electronic property, semiconductors are widely used in many electronic applications, especially in microprocessors and memory devices. It is regarded as foundation of modern microelectronics industry.

Silicon is a very important semiconductor material partly due to its unique crystal lattice structure and favorable band gap. It plays an irreplaceable role in microelectronics since it forms basis for a wide range of advanced integrated circuit (IC) applications.

With increased demands in technology, silicon based electronic devices are made smaller and smaller to satisfy the desired size and need for increased speed. While the decrease in size of silicon devices approaches the physical limit of silicon-based materials, molecular level electronics attracts interest from both the scientific and engineering communities. These studies aim to replace inorganic silicon based integrated circuits with electronically functional devices constructed by single molecule or a cluster of molecules. Creating a silicon-organic molecule interface has been very
popular area of research over the past decades. The organic molecules include biomolecules and polymers. By linking functional organic molecules to a silicon device, one can utilize both the selectivity of organic molecule, and the electronic properties of silicon itself.

In 1993, Linford and Chidsey first reported a method to attach organic molecules to silicon surfaces. Since then, a number of studies have been done to explore methods of attaching various functional molecules to silicon surfaces as well as characterization and application of modified silicon surfaces.
1.4 Methods of attaching organic molecule to silicon surfaces

1.4.1 Starting point

It’s worth mentioning that among several different silicon crystal structures, Si(100) and Si(111) are the most widely used silicon crystals. In an ideal situation, inside both Si(100) and Si(111) crystals, silicon atoms form a diamond cubic lattice structure. Four valence electrons of a silicon atom form four covalent bonds with adjacent silicon atoms, except for silicon atoms at the outmost layer, where each silicon atom only forms two covalent bonds with silicon atoms in the inner layer, leaving two electrons unpaired. Thus, this structure results in high surface free energy. Both Si(100) and Si(111) crystals will undergo a complicated reconstruction process and form structures with lower surface free energy. The most stable form of reconstructed surface structure for Si(100) and Si(111) are Si(100)-2 × 1 and Si(111)-7 × 7 surfaces, respectively.

Si(100)-2 × 1 can be best described as rows of Si–Si dimers while Si(111)-7 × 7 includes a more complex structure, both structures are shown in Figures 1.8 and 1.9.
Figure 1.8 Schematic of the Si(100) surface reconstruction. Left, ideal Si(100) surface, right, Si(100) 2 × 1 reconstructed surface. The large circles represent Si atoms in the outermost layer and the smaller black circles represent Si atoms in the second layer.
Although the silicon crystal reconstructs to lower the surface free energy, the surface silicon atoms still remain as active reaction sites. Without any treatment, silicon oxides will form on the silicon surface. The presence of oxides leads to an insulating surface that is not desired for many IC applications. It is also a problem for surface
modification because (1) Si-O bonds block silicon atoms, preventing the formation of stable, direct links with the substrate and (2) oxygen atoms form charge traps, which greatly affect the electronic properties of the target layers. Therefore, in most cases, the oxide layer must be removed before any further modification can be carried out on silicon surfaces. Also during the process of further modification, some preventive measures including inert gas environment, removal of dissolved oxygen from solutions must be done in order to prevent oxide layer formation.

In order to remove the surface oxides, a standard and mature 4-step RCA method\textsuperscript{23} was carried out. First, the silicon surface was treated with H\textsubscript{2}O\textsubscript{2} or a similar oxidant. This is to remove organic residues. Then the oxide layer on the silicon surface is removed by HF. The third step involves treating the silicon surface again with a mixture of HCl and H\textsubscript{2}O\textsubscript{2} with the purpose of removing ionic contamination. Lastly the silicon sample is etched by HF again and then rinsed by water to remove all remaining contaminants. Kato also reported the etching process can also be done by treating silicon surface with aqueous NH\textsubscript{4}F solution\textsuperscript{24}. Under UHV conditions, the oxide layer removal was done by exposing silicon surface to gas phase hydrogen in the presence of a hot tungsten filament at elevated surface temperature\textsuperscript{25}. After these treatments, a well ordered H-terminated silicon surface can be obtained and this H-terminated silicon surface is the most commonly seen starting point for silicon surface modification due to the relatively active H-termination site.

Similarly, Cl- terminated silicon surfaces are also reported\textsuperscript{26} as a starting point for silicon surface modification. The Cl- terminated silicon surfaces can be obtained by
treating H-terminated surfaces with a halogenation agent, and PCl$_5$ is the most common choice\textsuperscript{25}. In practice, PCl$_5$ is dissolved in chlorobenzene solution with a trace amount of benzoyl peroxide as initiator\textsuperscript{27}.

### 1.4.2 UHV or dry methods

As opposed to commonly adopted wet chemistry methods, a number of further modifications and attachments of targeting molecules to silicon surfaces can be done under UHV conditions. Existing literature reported exposure of clean H-terminated silicon surfaces to ammonia\textsuperscript{25}, tri-methyl-amine (TMA)\textsuperscript{28}, di-methyl-amine (DMA)\textsuperscript{28}, tri-ethyl-amine (TEA)\textsuperscript{29}, nitroalkane\textsuperscript{30}, azide\textsuperscript{31} and nitrobenzene\textsuperscript{32}. In these studies, ammonia or the amine undergo a chemisorption process on the silicon surface, followed by dissociation and insertion into the Si-H bond\textsuperscript{32}. Nitro-containing molecules attach to the silicon surface via various cycloaddition reactions\textsuperscript{33}.

### 1.4.3 Hydrosilylation of unsaturated molecules

Among the various wet chemistry methods, hydrosilylation of unsaturated molecules has gained extensive focus. There are different mechanisms behind hydrosilylation, including radical induced hydrosilylation, thermal hydrosilylation and photo-induced hydrosilylation.

When Linford and Chidsey first reported\textsuperscript{20} attaching organic molecules to a silicon surface, they explained that the initiation of the reaction was due to the
formation of carbon centered alkyl radical after introduction of peroxide initiator. The alkyl radical dehydrogenated H-terminated silicon surfaces, forming a silicon radical. This silicon radical actively reacts with an unsaturated bond to form Si-C covalent bond. The newly produced secondary alkyl radical dehydrogenates adjacent H-termination, yielding a chain reaction until the introduction of terminator. A schematic of this mechanism is shown as Figure 1.10 a. A disadvantage of this reaction was the addition of initiator and terminator inevitably introduces contamination into the system, potentially affecting subsequent reactions and surface properties.

Later while Chidsey and co-workers studied conditions for hydrosilylation, they discovered that the reaction could occur at elevated temperatures without the presence of an initiator. Currently thermal hydrosilylation is used widely because of the advantage that no initiator or terminator is required.

Another mechanism behind hydrosilylation is the electron-hole pair theory which helps to explain photo-induced hydrosilylation. In the past, it was believed that photo-induced hydrosilylation occurred under the same radical reaction mechanism; UV radiation breaks the Si-H bonds to form silicon radicals, their radicals then react with unsaturated bonds to form Si-C bonds. The energy of typical Si-H bond is around 3.5eV, thus the energy of UV light must exceed 3.5eV (wavelength <350nm) in order to break the Si-H bond. However, there are reports of visible light-induced hydrosilylation. Stewart used visible light with wavelength around 400nm to initiate hydrosilylation of alkenes and alkynes. Hamers reported a visible light (514 nm)-initiated modification of flat Si(111) and Si(001) surfaces by partial iodination. Sun reported attaching a variety
of unsaturated compounds on Si(100)-H surfaces by visible light (447 nm) at room temperature. This caused researchers to rethink the mechanism and Stewart\textsuperscript{35} proposed an exciton-mediated electrophilic-nucleophilic attack to explain the visible light-induced hydrosilylation. An unbound exciton produced by light absorption leads to a surface-localized supra-band gap positive charge (surface localized hole). This electrophilic surface charge was attacked by an alkene or alkyne nucleophile and formed a silylated $\beta$- carbocation upon Si-C bond formation. This carbocation can then abstract a hydride from an adjacent Si-H bond, yielding the neutral organic termination as detailed in Figure 1.10 b.
The discovery of photo-induced hydrosilylation provides the possibility of attaching various bio-molecules to the silicon surface under mild conditions, eliminating the need to heat the sample or introduce an initiator/terminator. In addition, photo-induced hydrosilylation enables selective modification at certain regions on the silicon
surface. Wayner\textsuperscript{38} pressed a gold mini-grid mask on Si(111)-H surface, and exposed that surface with UV light (254nm). The uncovered Si-H sites were oxidized while covered Si-H sites remained and were treated with 1-decene for further modification. Thus a silicon surface with both oxidized and alkylated regions was obtained. Both the AFM (atomic force microscopy) and CCD (charge-coupled device) images showed a distinct grid-shaped pattern of the surface. With the oxidized region being hydrophilic and alkylated region being hydrophobic, a surface with unique surface tension properties was obtained.

1.4.4 Alkylation of halogen-terminated surfaces.

Alkylation of halogen-terminated surfaces is another pathway to attach organic molecules to the silicon surfaces. Bansal first reported this method\textsuperscript{39} in 1996. First the H-terminated silicon is treated by a halogenation agent, such as PCl\textsubscript{5}, to form a Cl-terminated silicon surface. Then the Cl-termination is substituted by either an alkyl Grignard (RMgCl) or an alkyl lithium reagent (RLi). This substitution process is due to coupling between nucleophilic Si with a carbocation. A schematic of the alkylation reaction is shown in Figure 1.11.
Alkylation of halogen-terminated surfaces provides much flexibility for the introduction of organic molecules onto silicon surfaces. The alkylation reaction requires stringent control of reaction conditions (ie: no water, no oxygen) and can introduce various contaminants.

1.4.5 Direct alkylation of H-terminated surfaces

In addition to the two-step alkylation reactions, several direct alkylation reactions were reported. Boukherroub\textsuperscript{40} reported a direct linkage reaction between an alkyl Grignard (decylmagnesium bromide) and H-terminated surfaces. This approach reduces the alkylation process from 2 steps as discussed in section 1.4.4 to single step. It is believed that an electrochemical mechanism is involved\textsuperscript{41}. A schematic of this direct linkage is shown in Figure 1.12.
A similar direct alkylation reaction was reported by Liu\textsuperscript{42} using a Seyferth reagent (PhHgCCl\textsubscript{2}Br). Dichlorocarbene (\textsuperscript{1}CCl\textsubscript{2}) generated by decomposition of the Seyferth reagent inserted into the Si-H bond on the silicon surface to form a Si-CCl\textsubscript{2}H group. Interestingly, Si-CCl\textsubscript{2}H termination was not the only product, since PhHgCCl\textsubscript{2}Br provides abundant halogen atoms, Si-Cl is also present. Si-Br is also produced on the surface, which can be confirmed by various characterization methods. An illustration of the two parallel reactions is shown in Figure 1.13. Unlike most of the reactions, where the ultimate goal is to limit the product to only one distinct substance, in this work the author intentionally introduced two products; dichloromethyl-terminated silicon and halogen terminated silicon. As these two products differ in reactivity, multifunctional surfaces possessing both stable silicon-carbon and reactive silicon-halogen sites can be obtained. This approach could be used to prepare complicated organic-silicon hybrid systems.
Figure 1.13 Two possible pathways in the reaction of H-Si(111) with the Seyferth reagent, top: production of Si-C termination, bottom: production of Si-Halogen termination.

1.4.6 Electrochemical method

Electrochemical methods are commonly used in producing closely packed, well-ordered phenol based monolayers on Si(111) surfaces. Villeneuve reported depositing an aryl diazonium molecule onto the Si(111) surface. The process is cathodic and prevents any degradation or oxidation of the surface during surface processing. It leaves
the remaining sites passivated with hydrogen. A schematic of this reaction is shown in Figure 1.14.

Figure 1.14 Schematic of electro-deposition of aryl diazonium molecule on silicon surface.

1.4.7 Surface plasma induced polymerization

Plasma polymerization is an effective way to deposit fluoro-containing films on silicon surfaces. Neoh reported depositing allylpentafluorobenzene (APFB) onto the Si(100) surface with the presence of a plasma. A schematic of the polymerization process is shown in Figure 1.15.
Figure 1.15 Schematic of plasma induced polymerization of APFB (allylpentafluorobenzene) on silicon surface.
1.5 Characterization of silicon-based organic monolayers

1.5.1 Chemical composition

The chemical composition of silicon-based organic monolayers can be studied by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). A detailed introduction of the mechanism and instrumentation used in XPS will be discussed in section 1.7.

Auger electron spectroscopy is based on the Auger process, where a core shell electron is first removed by electron beam bombardment, leaving behind an electron hole. As this is an unstable state, the core hole can be filled by an outer shell electron, whereby the electron moving to the lower energy level loses an amount of energy equal to the difference in orbital energies. The transition energy can be coupled to a second outer shell electron, which will be emitted from the atom if the transferred energy is greater than the orbital binding energy. This process is illustrated in Figure 1.16.

![Figure 1.16 Schematic of Auger process.](image-url)
The kinetic energy of secondary emitted electron is measured by electron energy analyzer and thus information about the atom can be obtained. It provides information on elemental identification and some chemical information about the first 2-10 atomic layers. It’s also combined with ion beam sputtering to provide in-depth information to a depth of 0.1-1 μm.

1.5.2 Structure

FTIR is a powerful tool to examine the surface structure of modified silicon surfaces. FTIR studies can be carried out in two modes: Attenuated total reflectance (ATR) or diffuse reflectance. The FTIR spectrum provides information about the vibrational modes of a molecule. This information can help in identifying specific chemical bonds and the structure of the surface. The Chidsey group45 discovered the peak position of CH$_2$ group was affected by the order of surface, in a well-ordered surface, the symmetric and asymmetric stretch peak are positioned at 2851cm$^{-1}$ and 2918 cm$^{-1}$, respectively. While those numbers shifted to 2855cm$^{-1}$ and 2924cm$^{-1}$ on rough surface.

Other than FTIR, X-ray absorption spectroscopy (XAS) and vibrational Raman spectroscopy are also used to examine the surface structure. Wang46 used XAS to study the molecular orientation and order in the initial growth of copper phthalocyanine on Si(111) surface.
1.5.3 Thickness of film and surface coverage

A common method to determine film thickness is X-ray diffraction (XRD). Rittner reported\textsuperscript{47} the layer thickness for 4 different organic monolayers by XRD and subsequent curve fitting with a two layer model. The results are shown in Table 1.1. He concluded that thickness of this layer1 does not significantly vary between the different self-assembled monolayers (SAM). Layer 2, with a thickness value within the range of 22–33 Å depending on the type of the SAM associated with the organic monolayer itself, including the functional end group and the alkyl chain. In this case, the layer thickness increases as the size of the end group increases.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Layer 1 (Å)</th>
<th>Layer 2 (Å)</th>
<th>Layer 2 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTS</td>
<td>10.7</td>
<td>22.6</td>
<td>21.1</td>
</tr>
<tr>
<td>Thiophene</td>
<td>10.9</td>
<td>26.5</td>
<td>25.1</td>
</tr>
<tr>
<td>Phenoxy</td>
<td>10.9</td>
<td>26.4</td>
<td>26</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>10.7</td>
<td>32.4</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Table 1.1 Experimental thickness values (in Å) for layer 1 and layer 2 determined from the analysis of the x-ray reflectometry data, together with the simulated SAM thicknesses, for the various SAMs with different end groups\textsuperscript{47}. (OTS: octadecyltrichlorosilane: $\text{CH}_3(\text{CH}_2)_{18} – \text{SiCl}_3$)
Theoretical calculations and related computer software both assist the determination of film thickness. Aswal\textsuperscript{48} reported a theoretical approach to estimate the thickness of the monolayer using approximate lengths of chemical bonds along the molecular axis and tilt angle of the chain. For alkyl chain attached to H-terminated silicon surface, its length can be calculated by:

\[ t = 1.26 \times (n - 1) \times \cos \phi + 1.86 \]  \hspace{1cm} (1.2)

Where \( n \): number of carbon atom in the chain \( \phi \): tilt angle of the chain.

In addition to XRD, Rittner\textsuperscript{47} also performed simulations using Molecular Orbital PACkage (MOPAC) software. The results are shown in Table 1.1. Good agreement is found between the simulated layer 2 values and the experimental layer 2 thicknesses. It is believed that layer 1 was associated with the interface while layer 2 was associated with different end groups terminated at the alkyl chain.

XPS data is also used to estimate the film thickness. Hunger\textsuperscript{49} reported attaching benzene derivatives to the silicon surface and conducted XPS scans on the resulting surface. Then a ratio between the intensities of C(1s) peak and Si(2p) peak was calculated based on XPS spectrum of nitrobenzene, bromobenzene and methoxybenzene terminated silicon surfaces. That number was found to be 2.5 and 3.4 for nitro and bromobenzene, respectively. But the same number for methoxybenzene
terminated silicon surfaces is only 0.2. They concluded that the deposited bromobenzene and nitrobenzene layers were considerably thicker than that of the methoxybenzene process.

Quantitatively, they also introduced an equation below to estimate the thickness of the film:

\[
\frac{l_{C_{1s}}}{l_{Si2p}} = \frac{l_{C_{1s}}}{l_{Si2p}} \frac{1 - \exp(-d / \lambda_{C_{1s}}^0)}{1 - \exp(-d / \lambda_{Si2p}^0)}
\]  

(1.3)

Where \(l_{C_{1s}}, l_{Si2p}\): the C1s and Si2p photoelectron intensity of a clean, semi-infinite silicon crystal.

\(\lambda_{C_{1s}}, \lambda_{Si2p}\): the electron mean free path in the layer, 3.2nm and 3.6nm, respectively.

Based on this equation, the film thicknesses of nitrobenzene, bromobenzene and methoxybenzene terminated silicon surfaces were calculated as: 2.7-4.5nm, 3.4-5.3nm and 0.25-0.5nm, respectively.

If the organic functional group attached to the silicon surface contains electrochemical properties, the extent of coverage can be measured by cyclic voltammetry. Fabre\textsuperscript{50} attached ferrocene onto silicon surfaces. A cyclic voltammetry experiment was performed on the organic monolayer in a CH\textsubscript{3}CN + 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} electrolytic medium. At lower scan rates, the total amount of attached ferrocene units can be estimated at \((3.3-3.5) \times 10^{-10}\) mol / cm\textsuperscript{2} from the area under either the anodic or...
cathodic peak. This value corresponds to a surface coverage of 0.25-0.27 ferrocene per surface silicon atom considering that the atomic density of Si(111) is $7.8 \times 10^{14}$ atoms /cm$^2$.

1.5.4 Surface property

Both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) depend on the interaction between a surface and the probe. Thus the information is provided at the atomic level, regarding surface roughness and surface defects. Both STM and AFM are non-destructive methods, and the produced sample can be preserved during STM and AFM studies. Eves$^{51}$ and Berrie$^{52}$ used STM and AFM to examine the surface of H- terminated Si(111) surface.

1.5.5 Stability

The monolayer on a silicon surface needs to have good stability in order to be applied in molecular electronics. It should be resistant to heat and chemicals, and was evaluated under different conditions including high temperature, acidic and basic environments. The stability of a certain silicon surface can be evaluated by repeated examination of the surface by the above mentioned methods and subsequent analysis of results. Any changes in chemical composition, structure, surface roughness may be a result of an unstable surface.
1.5.6 Thermodynamic and computational study involved in silicon surface modification

Thermodynamic data was used to explain facts discovered during silicon surface modification as well as to predict the activity of various silicon terminations. According to existing thermodynamic data\(^5\), silicon dioxide has a heat of formation of -910.86 kJ/mol, and that number for silicon carbide and silicon nitride are -73.22 kJ/mol and -851 kJ/mol, respectively. That explains why silicon oxides are likely to be formed during the silicon surface modification and importance of removing silicon oxides throughout the modification process.

Above mentioned facts can also be explained by chemical bond energy, according to existing literature\(^5\). The average bond energy for Si-O bond is approximately 460 kJ/mol while this number is 318 kJ/mol for Si-C, 355 kJ/mol for Si-N and 222 kJ/mol for Si-Si.

A closer approach for thermodynamic data including bond length and bond energy for various silicon surfaces can be obtained by Gaussian simulation. Perrine\(^2\) performed computations for those thermodynamics data at the B3LYP/6-311G(d,p) level of theory using Gaussian 3.0 suit of programs. In her simulation, a Si\(_{15}H_{16}\) cluster was used to represent the Si(100) surfaces and the Si\(_{17}H_{22}\) cluster was used to represent the Si(111) surfaces. The results are shown in Table 1.2. According to this result, Si-H, Si-Cl and Si-NH\(_2\) bond energies are among the lowest bond energies, thus most of the methods the attaching step started with hydrogen, chlorine or amine terminated surfaces.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Surface Site</th>
<th>Si–X bond length (Å)</th>
<th>Si–X bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–Si(111)</td>
<td>H–Si</td>
<td>1.493</td>
<td>−351.9</td>
</tr>
<tr>
<td>H–Si(100) mono-H</td>
<td>H–Si</td>
<td>1.491</td>
<td>−354.6</td>
</tr>
<tr>
<td>H–Si(100) di-H</td>
<td>H–Si</td>
<td>1.488/1.490</td>
<td>−370.6</td>
</tr>
<tr>
<td>Cl–Si(111)</td>
<td>Cl–Si</td>
<td>2.116</td>
<td>−372.2</td>
</tr>
<tr>
<td>Cl–Si(100)</td>
<td>Cl–Si</td>
<td>2.098</td>
<td>−370.7</td>
</tr>
<tr>
<td>F–Si(111)</td>
<td>F–Si</td>
<td>1.647</td>
<td>−545.5</td>
</tr>
<tr>
<td>F–Si(100)</td>
<td>F–Si</td>
<td>1.64</td>
<td>−541.1</td>
</tr>
<tr>
<td>OH–Si(100) (dissociated H₂O)</td>
<td>OH–Si</td>
<td>1.683</td>
<td>−443.4</td>
</tr>
<tr>
<td>NH₂–Si(100) (dissociated NH₃)</td>
<td>NH₂–Si</td>
<td>1.743</td>
<td>−367.9</td>
</tr>
<tr>
<td>Si–NH–Si (bridged)</td>
<td>Si–NH–Si</td>
<td>1.76</td>
<td>−678.2</td>
</tr>
</tbody>
</table>

Table 1.2 Comparison of selected bond lengths and bond energies optimized by Gaussian25.
1.6 Applications of modified silicon surfaces

1.6.1 Molecular electronic devices

A system consisting of silicon semiconductor-organic monolayer-metal is of great interest by researchers who are designing molecular electronic devices. By connecting organic terminated silicon surface to a metal, researchers can evaluate the electronic properties of the organic terminated silicon surfaces. Bocking\textsuperscript{55} attached a trifluoroacetyl-protected alkenythiol onto H-terminated silicon surface by thermal hydrosilylation. After the trifluoro-protecting group was removed, a junction Si-C\textsubscript{11}H\textsubscript{22}-S-Hg and Si-C\textsubscript{11}H\textsubscript{22}-S-Au was obtained. In this junction, an alkyl chain was connected to the silicon surface via a Si-C bond, while the Hg/Au metal was connected to metal electrodes. This junction system can help researchers obtain information about current transport through saturated molecules.

1.6.1.1 Capacitors

Richter\textsuperscript{56} reported attaching various alcohols of different lengths (from C\textsubscript{20}H\textsubscript{41}OH to C\textsubscript{18}H\textsubscript{37}OH) onto silicon (111) by UV promoted method, and Al was deposited on the organic monolayer. By current-voltage (IV) and capacitance-voltage (CV) measurements, these Si-organic-metal systems were determined to be functioning similar to conventional capacitors and accumulated capacitance decreased with the increased length of carbon chain.
1.6.1.2 Molecular memory device

Molecular memory devices are proposed by attaching a redox molecule onto silicon surfaces. The different redox states can be implemented to store information. Liu\textsuperscript{57} attached porphyrin-based molecules onto Si(100) surfaces and the system exhibited redox behavior useful for information storage. The monomeric porphyrins attached to silicon surface shown in Figure 1.17 exhibit two accessible cationic states which were accessed by applying external potentials. This molecular memory device proved to have a relative long retention time and was stable under extremes of temperature (400°C) and large numbers of read-write cycles ($10^{12}$). An increased memory capacity can also be achieved by replacing the monomeric porphyrins with a more complex multi-porphyrin containing molecules.
Figure 1.17 Schematic of the Si-tethered porphyrins molecular memory.

1.6.1.3 Molecular field effect transistor (FET)

He$^{58}$ attached a series of molecules onto H-terminated silicon surfaces in a channel region of a transistor, the molecules ranged from strong π-electron donors to strong π-electron acceptors as shown in Figure 1.18. Therefore, the device conductance was systematically tuned in accordance with the electron-donating ability of the grafted molecules, which was attributed to the charge transfer between the device channel and the molecules. Then the electronic characteristics including drain current (ID) and
threshold voltage (VT) in pseudo metaloxide-semiconductor field-effect transistors (MOSFETs) can be controlled in a wide electronic range.

Figure 1.18 Schematic of a molecular field-effect transistor (FET). (Adapted from ref. 58)

1.6.1.4 Photochemical-Controlled Molecular Switch

Wen\textsuperscript{59} attached the azobenzene-containing compound, 4-nitro-4'-N,N-di(2-hydroxy propyl) aminoazobenzene (NHPA), onto Si(111) surfaces via Si-O bond. The
monolayer surface showed preferably chemical stability. Switchable photoisomerizability of azobenzene molecules on these modified surfaces was observed in response to alternating UV and visible light exposure as shown in Figure 1.19. The measured conductivity showed distinct differences with trans and cis forms of azobenzene compounds on modified Si(111) surfaces, making it potentially useful as a photochemical-controlled molecular switch.

Figure 1.19 Schematic of a switchable azobenzene molecule modified Si(111) surface.

1.6.2 Chemical and biomolecule sensors

1.6.2.1 Chemical sensor

Mitchell\textsuperscript{60} reported a silicon based oxygen sensor. Tert-butylhydrazine amine-de-modified undecylenic acid was attached to Si(111) surface through a multi-step modification of H-terminated surface as shown in Figure 1.20. Molecular oxygen absorbed onto the organic monolayer can act as an electron acceptor, with the charged O\textsuperscript{2-} species being able to induce band bending in the underlying semiconductor, triggering an electric field induced second harmonic (EFISH) response, indicative of charge trapping at the surface. The EFISH technique does not require additional
electrical contacts with the silicon surface, thus a simple oxygen sensor can be obtained with a very low detection limit.

Figure 1.20 Steps of attaching tert-butylhydrazine amide-modified undecylenic acid onto silicon surfaces.

1.6.2.1 Biomolecule sensor

Organic monolayers formed on silicon surfaces provide an environment similar to membranes in which biomolecules such as nucleic acids, enzymes, and cells can be
attached. These biomolecules are often selective for various biological activities. Signals can be transported via the organic monolayer and silicon base and transferred into electronic signals, yielding a system that can be used as a bio-sensor or bio-chips.

Strothe$^{61}$ first reported attaching thiol-modified DNA onto organic terminated surface via a SSMCC (sulfosuccinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate) cross-linker as shown in Figure 1.21. This opens up possibilities of conveniently study DNA-protein interactions.
Figure 1.21 Schematic of organic terminated silicon surface with DNA connectivity, UDA: 10-undecylenic acid, PL: electrostatically bound polylysine, SSMCC: sulfoacrylimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate.
1.7 X-ray Photoelectron Spectroscopy

1.7.1 Mechanism

XPS, also known as Electron spectroscopy for chemical analysis (ESCA) was invented by Kai Siegbahn in 1960s. It was based on the photoelectric effect in which electrons are emitted from matter (metals and non-metallic solids, liquids or gases) as a consequence of their absorption of energy from electromagnetic radiation of very short wavelength, such as visible or ultraviolet light. A schematic of photoelectron emission process is shown in Figure 1.22.

![Schematic of photoelectron emission process](image)

Figure 1.22 Schematic of photoelectron emission process.

Surface analysis by XPS is accomplish by irradiating a sample with monoenergetic soft x-rays and analyzing the energy of the detected electrons. Usually, Mg Kα.
(hv=1253.6 eV), Al Kα (hv=1486.6 eV) X-rays are used. These photons have limited penetrating power in a solid, on the order of 1-10 micrometers. They interact with atoms in the surface region, causing electrons to be emitted by the photoelectric effect. Since electrons have much lower escape depth, only photoelectrons from top 10nm of the surface can escape from the surface and potentially be detected by the electron energy analyzer. The energy of the emitted electrons is given by:

\[ KE = hv - (E_B + \Phi) \]  \hspace{1cm} (1.4)

Where KE: Kinetic Energy
\( hv \): Photon Energy
\( E_B \): Binding Energy
\( \Phi \): Work function, minimum energy required to eject an electron from the highest level into vacuum.

A XPS spectrum can be obtained by measuring the kinetic energy of above mentioned electrons and then plotting intensities of the ejected photoelectrons versus binding energy.

1.7.2 Qualitative analysis

Because each element has a unique set of binding energies, XPS can be used to identify elements in the surface region. Variations in the elemental binding energies (the chemical shifts) arise from the differences in the chemical potential and polarizability of
compounds due to change in the chemical bonding of the elements. These chemical shifts can be used to identify the chemical state of the materials being analyzed. It’s commonly believed that withdrawal of valence electron charge results in increase in binding energy. Figure 1.23 showed XPS spectrum of an organic molecule attached Si(100) surface, from the spectrum, characteristic photoelectron peaks of C, N, O and Si as well as Auger peaks of O and N can be observed.

Figure 1.23 XPS spectrum of an organic molecule attached Si(100) surface. KLL, a type of Auger transition where primary electron was ejected from K shell then Auger electron was ejected from L shell due to the movement of another L shell electron to K shell hole.
1.7.3 Quantitative analysis

The complete XPS spectrum of a material contains peaks that can be associated with the various elements (except H and He) present in the outer 10 nm of that material. The area under these peaks is related to the amount of each element present, as shown in the equation below:

\[ I_i = N_i \sigma_i \lambda_i K \]  

(1.5)

Where \( I_i \) = Intensity of photoelectron peak for element “\( i \)”

\( N_i \) = average atomic concentration of element “\( i \)” in the surface under analysis

\( \sigma_i \) = photoelectron cross-section (Scofield factor) for element “\( i \)”

\( \lambda_i \) = inelastic mean free path of a photoelectron from element “\( i \)”

\( K \) = all other factors related to quantitative detection of a signal (assumed to remain constant during experiment)

Therefore, by measuring the peak areas and correcting them for the appropriate instrumental factors, the percentage of each element can be obtained. The elemental concentration as atomic fraction for each sample surface can be calculated based on the following equation:

\[ n_i = (l_i / \sigma_i K E^{0.7}) / \sum (l_j / \sigma_j K E^{0.7}) \]  

(1.6)

Where \( n_i \) is the atomic fraction of element \( i \),
$I_{ij}$ is the area of peak $j$ from element $i$,

$\sigma_{ij}$ is the photoionization cross-section of peak $j$ from element $l$, and

$KE$ is the kinetic energy of peak $j$ from element $l$. 
1.8 Thesis overview

Two strategies for attaching a fluorophore to chemically modified Si (100) surfaces were described. The fluorophore, 3-bromophenyl 3-phenyl-2-propynoate was designed based on report by Jung. It was proved to be highly selective for Gold(III) ion. By attaching this fluorophore to silicon surfaces, one can utilize both the selectivity for Gold(III) ion and good electronic properties of silicon, making this device potentially useful for quick detection of Gold(III) ion with low detection limit.

The remaining chapters of this thesis include methods adopted to creating organic terminated silicon surface (Chapter 2) as well as the results for the characterization of the synthesized surface (Chapter 3).
1.9 Reference


Chapter 2: Experimental Methods

2.1 Determination of vapor pressure of ionic liquids

2.1.1 Apparatus set-up

The Knudsen effusion method was used to determine the vapor pressures and a schematic of the apparatus used in this study is shown as Figure 2.1. The vacuum system and cold trap were constructed of stainless steel. The lower part of the tube containing the sample cell was made of copper for more efficient heat transfer with the oil bath. The top part of the tube was made of stainless steel and was connected to a liquid nitrogen cold trap by a KF 25 vacuum flange. The other end of the liquid nitrogen cold trap was connected to the vacuum system. The tube along with the liquid nitrogen cold trap can be isolated from the vacuum system by a gate valve. This ensures the pressure inside the vacuum system was kept low even when the tube and nitrogen cold trap were removed for cleaning and sample loading / unloading. Thus the pressure inside the tube can be pumped down to desired range within adequate time. The pressure inside the vacuum system was maintained by a turbomolecular pump and the system pressure can be read from using a nude ion gauge. The base pressure of the system is $3 \times 10^{-7}$ Pa.
Before each experiment, 1.0g - 1.2g of a given sample was loaded into the stainless steel sample holder, and the mass of the sample along with the sample holder was recorded. The diameter of the hole in the lid of sample holder was measured using a binocular microscope. The sample holder was then placed in a tube that connected to the vacuum system. When the temperature of the sample holder was stable at the
desired temperature, the valve was opened to the vacuum system and timing was started. The pressure inside the tube dropped to the base pressure within 10 minutes.

The normal time for an experiment was 24 – 100 hrs and the run time was sample dependent. Liquid nitrogen was used to condense the vapor of sample to prevent contamination of the vacuum system. After a period of time, the sample was isolated from the vacuum system and was removed from the tube. After cooling to room temperature in a desiccator, the mass of sample holder was measured again to calculate the mass lost. Then the vapor pressure was calculated using equation 2.1;

\[
p = \frac{g}{At} \sqrt{\frac{2\pi RT}{M}} \tag{2.1}
\]

Where \( g \): mass loss \( A \): area of hole \( t \): time \( M \): molecular mass and \( T \): temperature.

All experiments used a temperature range of 373 K – 433 K. The mass of sample along with sample holder before and after each experiment is measured with an analytical balance that has a detection limit of \( \pm0.00001 \)g.

2.1.2 Method calibration

The vapor pressure of benzophenone (Sigma-Aldrich, 99%) was measured at several temperatures and compared to literature values to examine the reliability of the method. The results of Clarke and Glew\(^2\) are used for the literature comparison. The
vapor pressure of benzophenone was fit using equation 2.2 determined by these authors\textsuperscript{3}.

\[
R \ln \frac{P}{P_0} = - \frac{\Delta_c^0 G_m(\theta)}{\theta} + \frac{\Delta_c^0 \Delta h_m^0(\theta)(\frac{1}{\theta} - \frac{1}{T}) + \Delta_c^0 \Delta C_{p,m}(\theta)(\frac{\theta}{T} - 1 + \ln(\frac{T}{\theta}))}{\theta}
\]

(2.2)

Where \( P \): vapor pressure, \( P_0 \): selected reference pressure, \( \theta \): selected reference temperature, \( R \): gas constant, \( \Delta_c^0 G_m(\theta) \): the difference in molar Gibbs energy between the gaseous and the condensed phase at the selected reference pressure, \( \Delta_c^0 \Delta h_m^0(\theta) \): the difference in molar enthalpy between the gaseous and the condensed phase, and \( \Delta_c^0 \Delta C_{p,m}(\theta) \): the difference between the heat capacities of the perfect gas and of the condensed phase.

Holes with non-zero length lead to a reduction in the number of particles escaping the sample cell. Molecules may enter the hole, strike the hole wall, and go back into the sample cell space instead of going out into the vacuum. The “effective area” of the hole then becomes \( A f \), where \( f \) is a correction factor called the Clausing factor and depends on the ratio of hole length to hole radius. Iczkowski et al. determined the Clausing factors for cylindrical holes\textsuperscript{4}. Another approach to determine the effective area is to adjust the hole area by determining the hole area needed for the benzophenone calibration data to match the literature values. The adjusted hole areas from both approaches are \( 2.498 \times 10^{-7} \text{ m}^2 \) and \( 2.246 \times 10^{-7} \text{ m}^2 \), respectively. The hole area determined from matching literature value of benzophenone is 10% smaller compared
to the hole area determined using the Clausing factor. The effective hole area used for this study is the adjusted value used to match the literature values of Clarke and Glew. This adjusted effective hole area is then used in all the vapor pressure calculations.

2.1.3 Data collection and processing

Vapor pressure measurements were conducted for three different ionic liquid samples: tetraoctylammonium bis (2-ethyl hexyl) sulfosuccinate ([N8888][AOT]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide (([C4C1Im][NTf2]), and 1,3-bis(3-methylimidazolium-yl) propane bis(trifluoromethylsulfonylimide ([C3(C1Im)2][NTf22]). The structures of these three ionic liquids are shown as Figure 2.2. They were synthesized and purified by published methods5. It should be note that ionic liquids [C4C1Im][NTf2] and [C3(C1Im)2][NTf22] are similar in structure. Both of them are consist of similar imidazolium based cation and identical anion, which will help in exploring the relationship between structure of ionic liquid and its vaporization properties.

Each ionic liquid sample was loaded into the sample holder, then the sample holder was placed into vacuum system and heated without a lid, the purpose for this treatment is to further remove impurities from the ionic liquid sample. Then the vapor pressure data was collected over 3-4 different temperatures with replicate measurements.
Figure 2.2 Structure of three ionic liquid samples.
Vapor pressure data was then plotted as the natural logarithm of pressure versus reciprocal temperature. The enthalpy of sublimation of each sample was calculated based on the Clausius–Clapeyron relation (equation 2.3).

\[
\ln P_2 - \ln P_1 = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]  

(2.3)

Where \( P_1 \) and \( P_2 \): vapor pressures at temperature \( T_1 \) and \( T_2 \), respectively, \( \Delta H \): sublimation enthalpy and \( R \): The gas constant.
2.2 Organic synthesis

2.2.1 Synthesis of 3-bromophenyl 3-phenyl-2-propynoate

2.2.1.1 Material

All chemicals were reagent grade or better unless otherwise noted and used as received. The following chemicals were used: 3-bromophenol (Acros Organics, 99%), 3-phenyl-2-propynoic acid (Sigma-Aldrich, 99%), N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDC ∙ HCl, Sigma-Aldrich, 97%), hexane (Fisher, 99.9%), 4-(dimethylamino)pyridine (DMAP, Sigma-Aldrich, 99%), methylene chloride (Fisher, 99%) and ethyl acetate (Fisher, 99.9%, HPLC grade).

2.2.1.2 Synthesis procedure

3-bromophenyl 3-phenyl-2-propynoate was synthesized as follows (Figure 2.3). About 0.865g (5 mmol) of 3-bromophenol, 0.7307g (5 mmol) of 3-phenyl-2-propynoic acid, 0.956g (5mmol) of EDC ∙ HCl and 0.3665g (3mmol) of DMAP were mixed and dissolved in about 8ml of methylene chloride. This mixture was stirred at 0°C for 1 hour and then stirred at room temperature for 12 hours. Silica gel column chromatography was used to separate the desired product from the matrix and the elution solvent was a 1:4 mixture of ethyl acetate and hexane. A rotary evaporator was used to remove the organic solvent. The remaining product was stored in a capped vial filled with nitrogen for later use.
2.2.2 Synthesis of t-BoC-protected 11-amino-1-undecene

2.2.2.1 Material

All chemicals were reagent grade or better and used as received: 1-amino-10-undecene (Right Price Chemicals, 97%), chloroform (Sigma-Aldrich, 99.8%, HPLC grade), sodium bicarbonate (Fisher, 99.9%, ACS certified), sodium chloride (Fisher, 100.1%, ACS certified), di-tert-butyl dicarbonate (Aldrich, 99%, ACS Certified), diethyl ether (Fisher, 99.9%, ACS certified), magnesium sulfate (Fisher, 99.9%, ACS Certified).

2.2.2.2 Synthesis procedure

t-BoC-protected 11-amino-1-undecene was synthesized as follows (Figure 2.4). About 2.5 g of 1-amino-10-undecene was dissolved into 30 mL of chloroform and combined with 6% sodium bicarbonate solution which was made by dissolving about 1.5 g of NaHCO₃ in 25 mL of water. About 3.22 g of sodium chloride and 3.59 g of di-tert-butyl dicarbonate were dissolved in a few milliliters of chloroform. The two above-mentioned solutions were mixed in a round-bottom flask and refluxed at 90°C for 2
hours. After the reaction, the matrix was extracted twice with 50 mL of diethyl ether. The organic extracts were dried over magnesium sulfate, filtered, and diethyl ether was removed from the filtrate by a rotary evaporator. The remaining light-yellow colored product was then transferred into capped vial filled with nitrogen for later use.

![Chemical structure](image)

Figure 2.4 Synthesis of t-BoC-protected 11-amino-1-undecene

### 2.2.3 Characteristics of synthesized product

Synthesized 3-bromophenyl 3-phenyl-2-propynoate (BPPP) and t-BoC-protected 11-amino-1-undecene (t-BoC) samples were characterized by a Finnigan TSQ7000 triple-quadrupole mass spectrometer. For BPPP samples, the desorption-off-glass atmospheric pressure chemical ionization (APCI) method was used. For the t-BoC samples, the sample was dissolved in acetonitrile and directly infused in the ion source. Ionization was done by electrospray ionization (ESI). The t-BoC-protected 11-amino-1-undecene sample was also characterized using a Bruker ARX 250MHz NMR Spectrometer.

Synthesized 3-bromophenyl 3-phenyl-2-propynoate (BPPP) was observed in APCI-MS spectra as shown in Figure 2.5, the peaks at 300.91 and 302.92 represent protonated BPPP molecule with two different isotopes of bromine.
In the ESI-MS spectra shown in Figure 2.6, t-BoC-protected 11-amino-1-undecene was also observed in the peak at 292.10, suggesting the molecule was in the form of [M+Na]^+.

Figure 2.5 APCI mass spectrum of synthesized 3-bromophenyl 3-phenyl-2-propynoate.
Figure 2.6 ESI mass spectrum of synthesized t-BoC-protected 11-amino-1-undecene.

The H-NMR spectrum as shown in Figure 2.7 also suggests the presence of 3-bromophenyl 3-phenyl-2-propynoate, detailed below:

$^1$H NMR (3-bromophenyl 3-phenyl-2-propynoate 300K) $\delta$ 5.604-5.700 (m, 1H, NH$^-$), 4.800-4.807 (d, 3H, CH$_2$=CH$_2$), 2.94-2.96 (t, 2H, CH$_2$-N), 1.858-1.909 (m, 2H, CH$_2$=CH-CH$_2$), 1.133-1.391 (m, 23H, (-CH$_2$)$_7$ and -C(CH$_3$)$_3$).
Figure 2.7 H-NMR spectrum of synthesized t-BoC protected 11-amino-1-undecene.
2.3 Modification and functionalization of silicon semiconductor surfaces

2.3.1 Preparation of hydrogen terminated Si (100) surfaces

2.3.1.1 Material

All chemicals were reagent grade or better and used as received: hydrogen peroxide (Fisher, 30% ACS Certified), ammonium hydroxide (Fisher, 29.54%, ACS Certified), hydrochloric acid (Fisher, 36.5%-38%, ACS Certified), hydrofluoric acid (Fisher, 47%-51% ACS Certified), milli-Q water (18 MΩ). The silicon substrates were cleaved from 3” single-sided polished Si (100) wafers (Virginia Semiconductor, P-doped, 0.035-0.060 Ωcm).

Solution 1 (S1) was prepared from a mixture of 4:1:1 milli-Q water, hydrogen peroxide, and ammonium hydroxide, by volume. Solution 2 (S2) was a mixture of 4:1:1 milli-Q water, hydrogen peroxide, and hydrochloric acid, by volume.

2.3.1.2 Standard RCA (HF etching) procedure

The hydrogen-terminated Si (100) surface was prepared as follows (Figure 2.8). Two clean 250 mL Teflon beakers were filled with 90 mL of S1. Both beakers were heated to 80°C in a water bath. Nitrogen gas was bubbled through each solution for at least 30 minutes. The beakers were later removed from the water bath with all S1 disposed. After rinsing with milli-Q water several times, the beakers were cleaned and ready for following procedure.
The silicon sample is gently blown with nitrogen gas and rinsed with milli-Q water. The sample is then placed in above-mentioned Teflon beaker filled with S1. The beaker containing S1 and the sample were placed into the 80°C water bath for 10 minutes before the beaker was removed from the water bath and the silicon sample was rinsed several times with milli-Q water. Once there is oxide layer formed on the surfaces, hydrofluoric acid was added to another Teflon beaker and silicon wafer was immersed in hydrofluoric acid for about 2 minutes in order to remove the oxide layer along with the surface contaminants. Then the Si sample is removed and rinsed several times with milli-Q water. After that the silicon wafer was again transferred to a Teflon beaker containing enough S2 and was immersed. The beaker was placed in 80°C water bath for 10 minutes before it was removed from the water bath, and the silicon wafer was rinsed several times with milli-Q water. The final step is to etch the silicon wafer and create the hydrogen-terminated surface. Sufficient 48% concentrated hydrofluoric acid is added to the beaker to completely immerse the silicon sample and the sample is placed in the solution for 1 minute. After removal from the hydrofluoric acid, the silicon sample was rinsed several times with milli-Q water followed by blowing dry with a steam of dry nitrogen. Because H-terminated Si surfaces will oxidize slowly at atmospheric pressure, they were either placed into the vacuum chamber or further modified immediately after preparation.
Figure 2.8 Preparation of hydrogen terminated Si (100) surface by RCA procedure.

2.3.1.3 NH₄F buffer etching procedure

Instead of using hydrofluoric acid for final etching of the silicon samples, a NH₄F buffer solution (pH = 4) was used to treat the silicon samples (Figure 2.9). The NH₄F buffer was made by mixing 10mL of ammonium hydroxide and 3mL of hydrofluoric acid. The silicon sample was placed in the NH₄F buffer for 10 minutes before removed and rinsed milli-Q water several times. After blown dry with a steam of dry nitrogen, the silicon samples were either placed into the vacuum chamber or further modified immediately.

Figure 2.9 Preparation of hydrogen terminated Si (100) surface by NH₄F etching method.
2.3.2 NH$_3$/PCl$_5$ pathway

2.3.2.1 Material

All chemicals were reagent grade or better and used as received unless otherwise noted: phosphorus pentachloride (PCl$_5$, Sigma-Aldrich, 98%), benzoyl peroxide (Sigma-Aldrich, 97%), chlorobenzene (Acros Organics, 99.8%), ammonium hydroxide (Fisher, 14.8N ACS Certified), tetrahydrofuran (THF, Acros Organics, 99.9%), sodium tert-butoxide (NaOt-Bu, Acros Organics, 98%), bis(dibenzylideneacetone)palladium(0) (Pd(dba)$_2$, Sigma-Aldrich, 99%), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (RuPhos, Sigma-Aldrich, 95%), 3-bromophenyl 3-phenyl-2-propynoate (BPPP, self-synthesized, detailed in Chapter 2.2.1), milli-Q water (18 MΩ), hydrogen terminated Si (100) sample (freshly prepared, detailed in Chapter 2.3.1).

2.3.2.2 Preparation of chloride terminated Si (100) surfaces

1.2g of phosphorus pentachloride and 30mg of benzoyl peroxide were dissolved in 10 mL of chlorobenzene and then the solution was bubbled with nitrogen gas for 30 min to remove oxygen. The hydrogen terminated Si (100) sample was then immersed into the solution and placed in an oil bath at 105°C for 1 hour. After that the Si (100) sample was removed from the solution and rinsed with milli-Q water then dried under nitrogen flow.
2.3.2.3 Preparation of amine terminated Si (100) surfaces\textsuperscript{10}

5 mL of ammonium hydroxide was combined with 5 mL of tetrahydrofuran and this solution was bubbled with nitrogen gas for 30 min to remove oxygen. The chloride terminated Si (100) sample was then immersed into the solution and stirred at room temperature for 1 hour. After that the Si (100) sample was removed from the solution and rinsed with milli-Q water and dried under nitrogen flow.

2.3.2.4 Preparation of organic functional group terminated Si (100) surfaces\textsuperscript{11}

0.4805g (5 mmol) of NaOt-Bu, 0.0288g (0.05 mmol) of Pd(dba)\textsubscript{2}, 0.0233g (0.05 mmol) of RuPhos and 1 mL of BPPP were dissolved in 5 mL of tetrahydrofuran. The resulting mixture was bubbled with nitrogen gas for 10 min to remove oxygen. The
amine terminated Si (100) sample was then immersed into the solution and placed in an oil bath at 105°C for 30 min. After that the Si (100) sample was removed from the solution and rinsed with milli-Q water then dried under nitrogen flow.

Figure 2.12 Preparation of organic functional group terminated Si (100) surfaces.

2.3.3 t-BoC pathway

2.3.3.1 Material

All chemicals were reagent grade or better and used as received unless otherwise noted: t-BoC-protected 11-amino-1-undecene (t-BoC, self-synthesized, detailed in Chapter 2.2.1), methylene chloride (Fisher, 99%, ACS certified), ethyl ether (Fisher, 99.9%, ACS certified), methanol (Sigma-Aldrich, 99.9%, HPLC grade), trifluoroacetic acid (TFA, Sigma-Aldrich, 99%), ammonium hydroxide (Fisher, 29.54%, ACS Certified), toluene (Fisher, 99.9%, ACS certified), sodium tert-butoxide (NaOt-Bu, Acros Organics, 98%), bis(dibenzylideneacetone)palladium(0) (Pd(dba)₂, Sigma-Aldrich,
99%), 2-dicyclohexylphosphino-2',6'-diisoproxybiphenyl (RuPhos, Sigma-Aldrich, 95%), 3-bromophenyl 3-phenyl-2-propynoate (BPPP, self-synthesized, detailed in Chapter 2.2.1), milli-Q water (18 MΩ), hydrogen terminated Si (100) sample (freshly prepared, detailed in Chapter 2.3.1).

### 2.3.3.2 Preparation of t-BoC terminated Si (100) surfaces

About 3 mL of the t-BoC protected 11-amino-1-undecene was dissolved in 10 mL of methylene chloride. Then the solution was bubbled with nitrogen gas for 10 min to remove oxygen. The hydrogen terminated Si (100) sample was then immersed into the solution and placed in an oil bath at 105°C for 8 hours. The Si (100) sample was removed from the solution and cleaned in diethyl ether, methanol and methylene chloride. The sample was rinsed with milli-Q water and dried under nitrogen flow.

![Figure 2.13 Preparation of t-BoC terminated Si (100) surfaces.](image)
2.3.3.3 Preparation of amine terminated Si (100) surfaces

The t-BoC terminated Si (100) sample was immersed into a solution of 25% TFA in methylene chloride and stirred at room temperature for 1 hour. It is followed by a 5 min rinse with 25% NH₄OH solution to remove the t-BoC protecting group and to form the amine terminated surface. The surface was then rinsed with milli-Q water and dried under nitrogen flow.

![Diagram of amine terminated Si (100) surfaces]

Figure 2.14 Preparation of amine terminated Si (100) surfaces.

2.3.3.4 Preparation of organic functional group terminated Si (100) surfaces

0.24g (2.5 mmol) of NaOt-Bu, 0.0288g (0.05 mmol) of Pd(dba)₂, 0.0233g (0.05 mmol) of RuPhos and 1 mL of BPPP were dissolved in 10 mL of toluene. The resulting mixture was bubbled with nitrogen gas for 10 min to remove oxygen. The amine terminated Si (100) sample was then immersed into the solution and placed in an oil bath at 105°C for 1 hour. The Si (100) sample was removed from the solution and cleaned with methanol. The sample was then rinsed with milli-Q water and dried under nitrogen flow.
Figure 2.15 Preparation of organic functional group terminated Si (100) surfaces.
2.4 XPS analysis of modified Si (100) surfaces

2.4.1 Instrumentation

All of the modified Si (100) surfaces, including the intermediate products, were examined by the X-ray photoelectron Spectroscopy (XPS). XPS scans are performed using a VSW TA-10 X-ray source with a twin anode (Mg/Al). The Mg Kα anode is operated at 14.5 kV and 20 mA (290 Watts). The Mg Kα photon energy is 1253.6 eV. The Al Kα anode is operated at 14.5 kV and 30 mA (435 Watts). The Al Kα photon energy is 1486.6 eV.

The surface of the Si (100) samples was examined in an ultra-high vacuum environment. All experiments were performed in an ultra-high vacuum (UHV) system in order to eliminate the excessive surface contamination. The ultra-high vacuum system adopted multiple pumps and the base pressure for the system was $1 \times 10^{-10}$ torr.

The CMA (Cylindrical Mirror Analyzer) is operated at a fixed pass energy mode for XPS to measure the kinetic energy of the emitted electrons. A pass energy of 50 eV was used for high-resolution scans.

2.4.2 Data collection

A wide scan, comprising photoemission features from all components, and detailed scans of the individual elemental regions were collected with pass energies of 100 eV and 50 eV, respectively. For the wide scan, the spectra were measured in 1 eV intervals with a dwell time of 75 milliseconds and were averaged over 20 scans. For the
detailed scan, the spectra were measured in 0.05 eV intervals with a dwell time of 75 milliseconds, and were signal averaged for 50 scans for each elemental region.

2.4.3 Qualitative analysis of spectra

The data saved in a binary format by the AugerScan data acquisition software and was later processed in Casa XPS software. Wide scan spectra were used to determine an overall picture of the sample surfaces, while detailed spectra were fitted using a GL30 (Gaussian 70%–Lorentzian 30%) line shape, therefore information including the position, area, and FWHM (full width at half maximum) of each elemental peak can be extracted from the software. A qualitative study of those spectra was conducted with a main focus on chemical environment and chemical state of each element present on the surfaces.

2.4.4 Quantitative analysis of spectra

A quantitative analysis of spectra was also carried out. The elemental concentration as atomic fraction for each sample surface was calculated based on the following equation:

\[
n_i = \frac{(I_{ij} / \sigma_j KE^{0.7})}{\sum (I_{ij} / \sigma_j KE^{0.7})}
\]  

(2.4)

Where \( n_i \) is the atomic fraction of element \( i \),

\( I_{ij} \) is the area of peak \( j \) from element \( i \),
$\sigma_{ij}$ is the photoionization cross-section of peak $j$ from element $I$, and

$KE$ is the kinetic energy of peak $j$ from element $I$.

The major elements studied include carbon, oxygen, silicon and nitrogen. The change in the specific elemental percentage was studied to determine the extent of modification made to the surface. The composition of the sample surfaces during different stages of the surface modification were assessed based on the calculated elemental percentage, and then later compared with the stoichiometry of sample.
2.5 References

Chapter 3: Results and discussions

3.1 Determination of vapor pressure of ionic liquids

3.1.1 Method calibration

3.1.1.1 Benzophenone data

All benzophenone data is shown in Table 3.1. The results of Clarke and Glew\(^1\) are used for the literature comparison. The vapor pressure of benzophenone was fit using equation 3.1 determined by these authors\(^2\). The measured vapor pressures are consistently 10% larger than the literature value. The possible reason is due to different ways in which the hole area was corrected, thus a calibration of the method is done detailed in next section.

\[
R\ln\frac{P}{P_0} = -\frac{\Delta_{ca}G_m^0(\theta)}{\theta} + \Delta_{ca}H_m^0(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{ca}C_{P,m}^0(\theta)\left(\frac{\theta}{T^2} - 1 + \ln\left(\frac{T}{\theta}\right)\right)
\]  

(3.1)

Where \(P\): vapor pressure, \(P_0\): selected reference pressure, \(\theta\): selected reference temperature, \(R\): gas constant, \(\Delta_{ca}G_m^0(\theta)\): the difference in molar Gibbs energy between the gaseous and the condensed phase at the selected reference pressure, \(\Delta_{ca}H_m^0(\theta)\): the difference in molar enthalpy between the gaseous and the condensed phase, and \(\Delta_{ca}C_{P,m}^0(\theta)\): the difference between the heat capacities of the perfect gas and of the condensed phase.
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<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Mass lost (g)</th>
<th>Pressure measured (Pa)</th>
<th>Literature value (Pa)</th>
<th>Relative error</th>
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</tr>
</tbody>
</table>

Table 3.1 Results and literature values of benzophenone.

### 3.1.1.2 Hole area correction

Holes with non-zero length lead to a reduction in the number of particles escaping the sample cell. Molecules may enter the hole, strike the hole wall, and go back into the sample cell space instead of going out into the vacuum. The “effective area” of the hole then becomes $A_f$, where $f$ is a correction factor called the Clausing factor and depends on the ratio of hole length to hole radius. Iczkowski et al. determined the Clausing factors for cylindrical holes\(^3\). Another approach to determine the effective area is to adjust the hole area by determining the hole area needed for the benzophenone calibration data to match the literature values.

The adjusted hole areas from both approaches are $2.498 \times 10^{-7}$ m\(^2\) and $2.246 \times 10^{-7}$ m\(^2\), respectively. The hole area determined from matching literature value of benzophenone is 10% smaller compared to the hole area determined using the Clausing factor. The second hole area correction method is used, since it eliminates all systematic
errors associate with instrument, sample cell and errors when measuring the hole radius and length. The effective hole area used for this study is the adjusted value used to match the literature values of Clarke and Glew. This adjusted effective hole area is then used in all the vapor pressure calculations.

3.1.2 Tetraoctylammonium bis (2-ethyl hexyl) sulfosuccinate ([N8888][AOT])

Vapor pressure is measured at three different temperatures in the range of 403-423 K. At least two trials were done to ensure reproducibility. The pressure measured ranged from $1.4 \times 10^{-3}$ Pa to $5.8 \times 10^{-3}$ Pa. Complete results are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Mass lost (mg)</th>
<th>Pressure measured (Pa)</th>
</tr>
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<td>423</td>
<td>1416</td>
<td>2.2</td>
<td>$6.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>423</td>
<td>1460</td>
<td>1.9</td>
<td>$5.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 3.2 Vapor pressure data of Tetraoctylammonium bis (2-ethyl hexyl) sulfosuccinate.
The natural logarithms of measured pressures were plotted versus reciprocal of temperature to determine the enthalpy of sublimation. The results is shown in Figure 3.1, the ΔH determined is 108.7±13.7 kJ·mol⁻¹.

![Graph showing ln(P) vs 1/T](image)

Figure 3.1 Vapor pressure data plotting of Tetraoctylammonium bis (2-ethyl hexyl) sulfo succinate.

### 3.1.3 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄C₃Im][NTf₂])

Vapor pressure is measured at three different temperatures in the range of 373-403 K. The pressure measured ranged from 1.8×10⁻⁴ Pa to 3.3×10⁻³ Pa. Complete results are shown in Table 3.3.
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Mass lost (mg)</th>
<th>Pressure measured (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>6660</td>
<td>0.2</td>
<td>1.8×10^{-4}</td>
</tr>
<tr>
<td>383</td>
<td>6151</td>
<td>0.3</td>
<td>3.0×10^{-4}</td>
</tr>
<tr>
<td>393</td>
<td>4200</td>
<td>0.4</td>
<td>5.9×10^{-4}</td>
</tr>
<tr>
<td>398</td>
<td>3676</td>
<td>0.7</td>
<td>1.2×10^{-3}</td>
</tr>
</tbody>
</table>

Table 3.3 Vapor pressure data of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

The natural logarithms of measured pressures were plotted versus reciprocal of temperature to determine the enthalpy of sublimation. The results is shown in Figure 3.2, the ΔH determined is 88.9±14.1 kJ·mol⁻¹.
Figure 3.2 Vapor pressure data plotting of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

3.1.4 1,3-bis(3-methylimidazolium-yl) propane bis(trifluoromethylsulfonyl)imide ([C$_3$(C$_1$Im)$_2$][NTf$_2$]$_2$)

Vapor pressure is measured at three different temperatures in the range of 423-433 K. At least two trials were done to ensure reproducibility. The pressure measured ranged from $8.4 \times 10^{-4}$ Pa to $3.3 \times 10^{-3}$ Pa. Complete results are shown in Table 3.4.
Table 3.4 Vapor pressure data of 1,3-bis(3-methylimidazolium-yl) propane bis(trifluoromethylsulfonyl)imide.

The natural logarithms of measured pressures were plotted versus reciprocal of temperature to determine the enthalpy of sublimation. The results is shown in Figure 3.3, the ΔH determined is 192.5±26.8 kJ·mol⁻¹.
Figure 3.3 Vapor pressure data plotting of 1,3-bis(3-methylimidazolium-yl) propane bis(trifluoromethylsulfonyl)imide.

3.1.5 Overview and summary of ionic liquids data

According to Clausius–Clapeyron relation, a linear equation can be obtained between natural logarithms of measured pressures were plotted versus reciprocal of temperature, thus the vapor pressure at given temperature over the temperature range can be calculated. Vapor pressures at 400K is calculated based on measured data and is shown in Table 3.5.
<table>
<thead>
<tr>
<th></th>
<th>400K</th>
<th>Molar mass (g/mol)</th>
<th>ΔH (kJ/mol)</th>
<th>Vapor Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N8888][AOT]</td>
<td>888.5</td>
<td>108.7±13.7</td>
<td>9.5×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>[C₄C₁Im][NTf₂]</td>
<td>419.3</td>
<td>88.9±14.1</td>
<td>1.1×10⁻³</td>
<td></td>
</tr>
<tr>
<td>[C₃(C₁Im)₂][NTf₂]₂</td>
<td>766.6</td>
<td>192.5±26.8</td>
<td>3.5×10⁻⁵</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5 Vapor pressures and enthalpy of sublimations of three ionic liquids at 400K.

From data shown in Table 3.5, larger molecules have a lower vapor pressure and higher heats of vaporization within similar structure series, those properties significantly differ across ionic liquids with different structures.

The vapor pressure data determined is also compared with existing literature. Paulechka⁴ reported the vapor pressures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide over the temperature range between 457K and 517K. At 500K, the vapor pressure is reported as 0.18 Pa. While by extrapolating the linear equation shown in Figure 3.2, the vapor pressure at 500K is estimated to be 0.23 Pa based on the vapor pressure data reported in this thesis, which matches the literature data. The discrepancy between two vapor pressures is likely to be caused by change in enthalpies of vaporization over two temperature ranges.
3.2 Hydrogen terminated Si(100) surfaces

X-ray photoelectron spectroscopy (XPS) is used to examine the prepared surfaces on Si(100). All subsequent analyses are conducted based on XPS spectra. Details of the methods are included in Section 2.4.

3.2.1 Elemental analysis

A XPS full scan of the H-Si(100) sample is shown in Figure 3.4. Intense and sharp silicon peaks can be observed, as well as short carbon and oxygen peaks.

Figure 3.4 XPS spectrum of H-Si(100) surface.

A detailed elemental specific scan of Si(2p) region is shown in Figure 3.5. The Si(2p) peak is positioned at binding energy of 95 eV, that reveals that majority of silicon
atoms have a binding energy corresponding to elemental silicon. Since very limited silicon signal can be observed at around 99 eV which correspond to silicon (IV), there is very little silicon oxide on the surface.

![Figure 3.5 Si(2p) spectrum of the H-Si(100) surface.](image)

### 3.2.2 Quantitative analysis

H-Si(100) samples are prepared using two different passivation agents, HF and an acidic NH₄F buffer. The elemental percentages of C, N, O, Si of two samples are
shown and compared in Table 3.6. Despite the method suggested by Kato\textsuperscript{5}, NH\textsubscript{4}F etching results in a well-ordered silicon surface, there is nearly no difference between the samples prepared using different passivation agents from the quantitative perspective. On both silicon surfaces, majority of the surface consists of elemental silicon with little carbon and oxygen contamination. These surfaces provide an abundance of reactive H-Si sites for further modification. All subsequent modifications are conducted based on H-Si(100) surfaces prepared by HF etching method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Si(100) by HF etching</td>
<td>16%</td>
<td>2%</td>
<td>8%</td>
<td>74%</td>
</tr>
<tr>
<td>H-Si(100) by NH\textsubscript{4}F etching</td>
<td>17%</td>
<td>2%</td>
<td>8%</td>
<td>73%</td>
</tr>
</tbody>
</table>

Table 3.6 Elemental percentages of two H-Si(100) samples prepared using different passivation agents. Uncertainty for all percentages: ±1%

3.3 PCl\textsubscript{5}/NH\textsubscript{3} pathway

There are two intermediate silicon surfaces, Cl-terminated Si(100) and amine-terminated Si(100) along the PCl\textsubscript{5}/NH\textsubscript{3} modification pathway, as well as final product Org-Si(100) surface. A schematic of these three different silicon surfaces are shown in Figure 3.6. XPS spectra are obtained on three different silicon surfaces, then plotted and compared for qualitative analysis, by each element. A quantitative analysis is also conducted to examine the elemental fraction on the three different surfaces. The
elemental fraction information of Org-Si(100) surface is also further compared with the stoichiometry of desired product.

Figure 3.6 Schematic of three silicon surfaces obtained during the PCl5/NH3 pathway modification.

3.3.1 Carbon

XPS C(1s) spectra of Cl-Si(100), Amine-Si(100) and Org-N-Si(100) samples are shown in Figure 3.7. As shown in Figure 3.7, the C(1s) intensity significantly increased during the step when the organic molecule is attached to silicon surface. Main contributors of carbon on both Cl-Si(100) and Amine-Si(100) surfaces are carbon contaminations.
3.3.2 Nitrogen

XPS N(1s) spectra of the Cl-Si(100), Amine-Si(100) and Org-N-Si(100) samples are shown in Figure 3.8. A N(1s) peak is only observed for the Amine-Si(100) surface, while no peak is observed for the Cl-Si(100) or Org-Si(100) surfaces. This is due to the –NH termination on top of the Amine-Si(100) sample, while there is no nitrogen on Cl-Si(100)
sample. On Org-N-Si(100) sample surface, the nitrogen atoms are covered and shield by long carbon chain after the organic molecules are attached. This results in a reduced number of electrons ejected and detected by XPS and is the probable cause of no nitrogen signal being observed in the N(1S) region. The significant increase in nitrogen signal on the amine terminated surface confirms substitution by amine during the amination step.

![N(1s) spectra of the Cl-Si(100)(red), Amine-Si(100)(green) and Org-N-Si(100)(magenta) surfaces.](image)

Figure 3.8 N(1s) spectra of the Cl-Si(100)(red), Amine-Si(100)(green) and Org-N-Si(100)(magenta) surfaces.
### 3.3.3 Chlorine

XPS Cl(2p) spectra of the Cl-Si(100), Amine-Si(100) and Org-N-Si(100) samples are shown in Figure 3.9. A peak is observed in Cl(2p) region for the Cl-Si(100) surface, while no intensity is seen for the other two samples. This is due to the –Cl termination on top of the Cl-Si(100) sample. The reduction in Cl signal also confirms the Cl-terminations are substituted by amine during the amination step.

![Cl(2p) spectra](image)

Figure 3.9 Cl(2p) spectra of the Cl-Si(100)(red), Amine-Si(100)(green) and Org-N-Si(100)(magenta) surfaces.
3.3.4 Oxygen

XPS O(1s) spectra of Cl-Si(100), Amine-Si(100) and Org-N-Si(100) samples are shown in Figure 3.10. During the surface modification process, the silicon surface inevitably contacts with air thus oxides may form on the silicon surface. The stepwise increase of oxygen signal corresponds to the increased presence of surface oxides. Chemical shifts can also be observed on O(1s) region of Org-N-Si(100) surface. The attachment of organic molecule results in an larger oxygen signal and the peak position shifts to higher binding energy, which is due to the oxygen atoms in the organic molecule are in an ester functional group (-OC[=O]-). A peak fitting of the Org-N-Si(100) spectrum reveals that both oxygen atoms in the organic molecule (component 1, binding energy around 535eV) and oxygen atoms in surface oxides (component 2, binding energy around 534eV) contributes to the oxygen signal. The oxygen component 2 matches well the oxygen peak of Cl-Si(100) and Amine Si(100) samples. The distribution of these two different groups of oxygen is discussed in Section 3.4.7.
Figure 3.10 O(1s) spectra of the Cl-Si(100)(red), Amine-Si(100)(green) and Org-N-Si(100)(magenta) surfaces. Left, overlay of three spectra. Right, overlay of three spectra with the Org-N-Si(100) peak fitted.

3.3.5 Silicon

XPS Si(2p) spectra of the Cl-Si(100), Amine-Si(100) and Org-N-Si(100) samples are shown in Figure 3.11. The ratio between Si (IV) and Si (0) of three surfaces are roughly 0.5:1, 1:1 and 1.5:1, respectively. While the elemental silicon signal is slightly reduced
during the modification process, there is a significant increase in Si (IV) peak. That means a considerable portion of silicon surface is oxidized.

Figure 3.11 Si(2p) spectra of the Cl-Si(100)(red), Amine-Si(100)(magenta) and Org-N-Si(100)(green) surfaces.

### 3.3.6 Elemental percentage of different silicon surfaces

The elemental fractions on three different surfaces, as well as H-Si(100) surfaces is shown in Table 3.7. A stepwise decrease of the silicon fraction and the increase of oxygen fraction is observed and was discussed in previous section. The changes in
nitrogen and chlorine fraction proved the -Cl and amine groups are successfully attached to the surface and then removed. A significant increase in carbon fraction during the last step is due to attachment of organic molecule.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>N</th>
<th>Cl</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Si(100)</td>
<td>16±1%</td>
<td>2±0.3%</td>
<td>0%</td>
<td>8±1%</td>
<td>74±1%</td>
</tr>
<tr>
<td>Cl-Si(100)</td>
<td>13±5%</td>
<td>0%</td>
<td>5±3%</td>
<td>19±3%</td>
<td>62±5%</td>
</tr>
<tr>
<td>Amine-Si(100)</td>
<td>11±4%</td>
<td>2±1%</td>
<td>1±1%</td>
<td>27±4%</td>
<td>59±1%</td>
</tr>
<tr>
<td>Org-N-Si(100)</td>
<td>37±5%</td>
<td>1±1%</td>
<td>1±1%</td>
<td>31±3%</td>
<td>30±1%</td>
</tr>
</tbody>
</table>

Table 3.7 Elemental fractions of the H-Si(100), Cl-Si(100), Amine-Si(100) and Org-N-Si(100) surfaces.

3.3.7 Stoichiometry of the surface and its comparison to desired product

A representative result of quantitative analysis of the Org-N-Si(100) surface is shown in Table 3.8. For C, O and Si, multiple components are found using the peak fitting functions from Casa XPS. As discussed in previous sections, different C, O and Si sources contribute to the peak, each component corresponds to a certain group of C, O or Si atoms in the same or similar chemical environments. Based on this result, the stoichiometry of the surface can be further studied. First, the surface structure is represented with a scheme as shown in Figure 3.12. A small portion of silicon surface is
covered by silicon oxides (represented by SiO₂) while rest of silicon atoms connected to organic molecule via the -N- bond.

<table>
<thead>
<tr>
<th>Org-N-Si(100)</th>
<th>C(1s)</th>
<th>N(1s)</th>
<th>Cl(2p)</th>
<th>O(1s)</th>
<th>Si(2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cₐ</td>
<td>Cₜ</td>
<td>Oₐ</td>
<td>Oₜ</td>
<td>Siₐ</td>
</tr>
<tr>
<td>Peak position (eV)</td>
<td>285</td>
<td>286</td>
<td>402</td>
<td>198</td>
<td>534</td>
</tr>
<tr>
<td>Peak area</td>
<td>1087</td>
<td>299</td>
<td>73.9</td>
<td>45.5</td>
<td>2143</td>
</tr>
<tr>
<td>Atomic fraction</td>
<td>29%</td>
<td>8%</td>
<td>1%</td>
<td>1%</td>
<td>25%</td>
</tr>
<tr>
<td>Elemental fraction</td>
<td>37%</td>
<td>1%</td>
<td>1%</td>
<td>31%</td>
<td>30%</td>
</tr>
</tbody>
</table>

Table 3.8 A representative result from quantitative XPS analysis of the Org-N-Si(100) surface.

Figure 3.12 Schematic of the Org-N-Si(100) surface.
A detailed component assignment is shown in Table 3.9. Carbon atoms in the organic molecule can be group into two categories, unsaturated carbon atoms and carbon atoms on the saturated chain. Due to higher electron density around unsaturated carbon, the binding energy is slightly smaller than that of carbon in saturated chain. The atomic percentage of both carbon groups are 29% and 8%, respectively, roughly 4:1 ratio. As the numbers of carbon atoms in both groups are 12 and 3, the atomic percentage matches the stoichiometry of desired silicon surface with organic molecule attached.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak Assignment</th>
<th>Binding energy(eV)</th>
<th>Atomic percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Aromatic(4+6), Triple bond (2)</td>
<td>285.2</td>
<td>29 %</td>
</tr>
<tr>
<td></td>
<td>C-N(1), O-C(1), O-C=O(1)</td>
<td>286.3</td>
<td>8 %</td>
</tr>
<tr>
<td>O</td>
<td>O-C=O</td>
<td>535.0</td>
<td>6 %</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>534.8</td>
<td>25 %</td>
</tr>
<tr>
<td>Si</td>
<td>SiO₂</td>
<td>99.1</td>
<td>11 %</td>
</tr>
<tr>
<td></td>
<td>Elemental Si</td>
<td>95.1</td>
<td>19 %</td>
</tr>
<tr>
<td>N</td>
<td>-N-</td>
<td>401.6</td>
<td>1 %</td>
</tr>
</tbody>
</table>

Table 3.9 Elemental analysis and assignment of the Org-N-Si(100) surface.
3.4 t-BoC pathway

There are two intermediate silicon surfaces, t-BoC-R-Si(100) and Amine-R-Si(100) along the t-BoC modification pathway, as well as final product Org-R-Si(100) surface, where R represents a carbon chain consisting of 11 carbon atoms. A schematic of these three different silicon surfaces is shown in Figure 3.13. XPS spectra are obtained on three different silicon surfaces, then plotted and compared for qualitative analysis, by each element. A quantitative analysis is also conducted to examine the elemental fraction on three different surfaces. The elemental fraction information of Amine-R-Si(100) and Org-R-Si(100) surface are also further compared with the stoichiometry of desired products.
Figure 3.13 Schematic of three silicon surfaces obtained during the t-BoC pathway modification.
3.4.1 Carbon

XPS C(1s) spectra of the t-BoC-R-Si(100), Amine-R-Si(100) and Org-R-Si(100) surfaces are shown in Figure 3.14. As can be observed from the spectra, the C(1s) intensity increased during the modification, and details regarding contributors of carbon signal is discussed in Sections 3.5.6 and 3.5.7.

Figure 3.14 C(1s) spectra of the t-BoC-R-Si(100)(red), Amine-R-Si(100)(green) and Org-R-Si(100)(magenta) surfaces.
3.4.2 Nitrogen

XPS N(1s) spectra of the t-BoC-R-Si(100), Amine-R-Si(100) and Org-R-Si(100) surfaces are shown in Figure 3.15. A peak is observed in all spectra since all three surface structures contain nitrogen atoms. Note that the baseline of Amine-R-Si(100) spectrum is slightly lower than the other spectra, but the nitrogen peak is still visible and area of the nitrogen peaks are similar.

![Figure 3.15 N(1s) spectra of the t-BoC-R-Si(100) (red), Amine-R-Si(100) (green) and Org-R-Si(100) (magenta) surfaces.](image)

Figure 3.15 N(1s) spectra of the t-BoC-R-Si(100) (red), Amine-R-Si(100) (green) and Org-R-Si(100) (magenta) surfaces.
3.4.3 Oxygen

XPS O(1s) spectra of the t-BoC-R-Si(100), Amine-R-Si(100) and Org-R-Si(100) surfaces are shown in Figure 3.16. During the surface modification process, the silicon surface inevitably contacts with air, thus oxides may form on the silicon surface. The stepwise increase of oxygen signal corresponds to increased surface oxides. There is a small increase in oxygen signal from t-BoC-R-Si(100) to Amine-R-Si(100), which account for both the removal of oxygen containing t-BoC group as well as surface oxidization.

Figure 3.16 O(1s) spectra of the t-BoC-R-Si(100)(red), Amine-R-Si(100)(magenta) and Org-R-Si(100)(green) surfaces.
3.4.4 Silicon

XPS Si(2p) spectra of the t-BoC-R-Si(100), Amine-R-Si(100) and Org-R-Si(100) surfaces are shown in Figure 3.17. The decrease in elemental Si peak (binding energy=94 eV) intensity is due to organic molecule coverage on top of the silicon surface. While the slight increase in Si (IV) peak (binding energy=98 eV) indicates a portion of silicon surface is oxidized.

Figure 3.17 Si(2p) spectra of the t-BoC-R-Si(100)(red), Amine-R-Si(100)(green) and Org-R-Si(100)(magenta) surfaces.
3.4.5 Elemental percentage of different silicon surfaces

The elemental fraction on three different surfaces, as well as H-Si(100) surface, is shown in Table 3.10. The increased in carbon fraction proved the attachment of organic molecules, t-BoC protected 11-amino-1-undecene and 3-bromophenyl 3-phenyl-2-propynoate in first step and third step, respectively. Despite removal of the t-BoC protecting group during step 2, the carbon fraction increased, this is due largely to the decrease of the silicon fraction from t-BoC-R-Si(100) to Amine-R-Si(100). A significant decrease in silicon fraction is also shown, which is due to most of the silicon surface being covered by organic molecules during the modification, the number of ejected electrons from silicon atoms is reduced due to increased escape depth. The nitrogen and oxygen fractions are relatively stable during the modification.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Si(100)</td>
<td>16±1%</td>
<td>2±1%</td>
<td>8±1%</td>
<td>74±1%</td>
</tr>
<tr>
<td>t-BoC-R-Si(100)</td>
<td>41±3%</td>
<td>1±1%</td>
<td>17±2%</td>
<td>41±3%</td>
</tr>
<tr>
<td>Amine-R-Si(100)</td>
<td>59±3%</td>
<td>5±1%</td>
<td>17±2%</td>
<td>20±3%</td>
</tr>
<tr>
<td>Org-R-Si(100)</td>
<td>70±1%</td>
<td>5±1%</td>
<td>12±1%</td>
<td>13±1%</td>
</tr>
</tbody>
</table>

Table 3.10 Elemental fractions of the t-BoC-R-Si(100), Amine-R-Si(100) and Org-R-Si(100) surfaces.
3.4.6  Stoichiometry of the Amine-R-Si(100) surface and its comparison to desired product

A representative result of quantitative analysis of the Amine-R-Si(100) surface is shown in Table 3.11. For C and Si, multiple components are found using the peak fitting functions from Casa XPS\textsuperscript{6}. As discussed in previous sections, different C and Si sources contribute to the peaks, each component corresponds to a certain group of C or Si atoms in the same or similar chemical environments. Based on this result, the stoichiometry of the surface can be further studied. First, the surface structure is represented with a scheme as shown in Figure 3.18. A small portion of silicon surface is covered by silicon oxides (represented by SiO\(_2\)) while rest of silicon atoms connected to organic molecule via the long carbon chain.

<table>
<thead>
<tr>
<th>Amine-R-Si(100)</th>
<th>C(1s)</th>
<th>N(1s)</th>
<th>O(1s)</th>
<th>Si(2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C_A)</td>
<td>(C_B)</td>
<td>(O)</td>
<td>(Si_A)</td>
</tr>
<tr>
<td>Peak position (eV)</td>
<td>285.3</td>
<td>286.6</td>
<td>401.8</td>
<td>535.3</td>
</tr>
<tr>
<td>Peak area</td>
<td>1871.2</td>
<td>523.1</td>
<td>390.1</td>
<td>1559.3</td>
</tr>
<tr>
<td>Atomic fraction</td>
<td>45 %</td>
<td>12 %</td>
<td>6 %</td>
<td>15 %</td>
</tr>
<tr>
<td>Elemental fraction</td>
<td>57 %</td>
<td>6 %</td>
<td>15 %</td>
<td>22 %</td>
</tr>
</tbody>
</table>

Table 3.11 A representative result from quantitative XPS analysis of the Amine-R-Si(100) surface.
Figure 3.18 Schematic of Amine-R-Si(100) surface.

A detailed component assignment is shown in Table 3.12. Carbon atoms in the organic molecule can be grouped into two categories, carbon atoms at the both terminations of the chain and carbon atoms within the chain. Due to lower electron density around carbons at both terminations, the binding energy is slightly higher than that of carbon within the chain. The atomic percentage of both carbon groups are 12% and 45%, respectively. As the numbers of carbon atoms in both groups are 2 and 9, the atomic percentage matches the stoichiometry of desired silicon surface with organic molecule attached.
<table>
<thead>
<tr>
<th>Element</th>
<th>Peak Assignment</th>
<th>Binding energy(eV)</th>
<th>Atomic Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C-C(9)</td>
<td>285.3</td>
<td>45 %</td>
</tr>
<tr>
<td></td>
<td>C-Si(1), C-N(1)</td>
<td>286.6</td>
<td>12 %</td>
</tr>
<tr>
<td>O</td>
<td>SiO₂</td>
<td>535.3</td>
<td>15 %</td>
</tr>
<tr>
<td>Si</td>
<td>SiO₂</td>
<td>97.8</td>
<td>7 %</td>
</tr>
<tr>
<td></td>
<td>Elemental Si</td>
<td>94.4</td>
<td>15 %</td>
</tr>
<tr>
<td>N</td>
<td>-NH₂</td>
<td>401.8</td>
<td>6 %</td>
</tr>
</tbody>
</table>

Table 3.12 Elemental analysis and assignment of the Amine-R-Si(100) surface.

3.4.7 Stoichiometry of the Org-R-Si(100) surface and its comparison to desired product

A representative result of quantitative analysis of the Org-R-Si(100) surface is shown in Table 3.13. For C and Si, multiple components are found using the peak fitting functions from Casa XPS®. As discussed in previous sections, different C, O and Si sources contribute to the peaks, and each component corresponds to a certain group of C, O or Si atoms in the same or similar chemical environments. Based on these results, the stoichiometry of the surface can be further studied. First, the surface structure is represented with a scheme as shown in Figure 3.19. A small portion of silicon surface is covered by silicon oxides (represented by SiO₂) while rest of silicon atoms connected to organic molecule via the long carbon chain.
### Table 3.13 A representative result from quantitative XPS analysis of the Org-R-Si(100) surface.

<table>
<thead>
<tr>
<th>Si-Org</th>
<th>C(1s)</th>
<th>N(1s)</th>
<th>O(1s)</th>
<th>Si(2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>Peak position (eV)</td>
<td>285.2</td>
<td>285.7</td>
<td>285.8</td>
<td>287.6</td>
</tr>
<tr>
<td>Peak area</td>
<td>1624.3</td>
<td>350.5</td>
<td>845.6</td>
<td>244.8</td>
</tr>
<tr>
<td>Atomic fraction</td>
<td>38 %</td>
<td>8 %</td>
<td>20 %</td>
<td>6 %</td>
</tr>
<tr>
<td>Elemental fraction</td>
<td>71 %</td>
<td>4 %</td>
<td>13 %</td>
<td>12 %</td>
</tr>
</tbody>
</table>
Figure 3.19 Schematic of Org-R-Si(100) surface.
A detailed component assignment is shown in Table 3.14. Carbon atoms in organic molecule can be grouped into four categories, unsaturated carbon atoms, carbon atoms at the both terminations of the chain, carbon atoms within the chain and carbon atoms in ester structure. The binding energies of four different groups of carbon range from 285.2 eV to 287.6 eV, due to decreased electron density. The atomic percentages of carbon in four groups are 38%, 8%, 20% and 6%, respectively. As the numbers of carbon atoms in four groups are 12, 3, 9 and 2, the atomic percentage matches the stoichiometry of desired silicon surface with organic molecule attached.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak Assignment</th>
<th>Binding energy(eV)</th>
<th>Atomic percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Aromatic (4+6), Triple bond (2)</td>
<td>285.2</td>
<td>38 %</td>
</tr>
<tr>
<td></td>
<td>C-Si(1), C-N(2)</td>
<td>285.7</td>
<td>8 %</td>
</tr>
<tr>
<td></td>
<td>C-C(9)</td>
<td>285.8</td>
<td>20 %</td>
</tr>
<tr>
<td></td>
<td>O-C(1), O-C=O(1)</td>
<td>287.6</td>
<td>6 %</td>
</tr>
<tr>
<td>O</td>
<td>O-C=O</td>
<td>537.3</td>
<td>2 %</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>535.5</td>
<td>13 %</td>
</tr>
<tr>
<td>Si</td>
<td>SiO₂</td>
<td>98.2</td>
<td>5 %</td>
</tr>
<tr>
<td></td>
<td>Elemental Si</td>
<td>94.4</td>
<td>7 %</td>
</tr>
<tr>
<td>N</td>
<td>-NH-</td>
<td>401.9</td>
<td>4 %</td>
</tr>
</tbody>
</table>

Table 3.14 Elemental analysis and assignment of the Org-R-Si(100) surface.
3.5 A comparison between two methods

As shown and discussed in Sections 3.5 and 3.6, both PCl₅/NH₃ and t-BoC pathways are useful strategies of attaching organic molecules onto silicon surface.

From the experimental prospective, both strategies involve multi-step modifications of H-terminated Si(100) surface to Si(100) surfaces with reactive amine termination. Then a halogen containing organic molecule is attached to the amine termination through amination reaction. Each strategy requires rinsing and cleaning of the silicon surface after each step, thus the oxidization of surface becomes inevitable. However, the oxidization of surface can be controlled by shortening the time the silicon surface exposed to air and removing air from solution being used. In both methods, cross-linkers are used to initiate the amination reaction, thus introduced surface contamination.

As shown from the quantitative XPS analysis of the products, the modification by t-BoC pathway appears to be more complete, as indicated by a lower silicon fraction and higher carbon fraction of the final product. This can be also explained based on the different structures of the product, on Org-R-Si(100) surfaces, organic molecules connect to the silicon surface via long carbon chain while on Org-N-surfaces, organic molecules connect to the silicon surface via -N- bond. The latter will be largely influenced by the space hindrance thus the coverage rate is lower than former.

Silicon surfaces obtained along the t-BoC pathway also appears to be relative stable to oxygen, as indicated by a lower oxygen atomic percentage of the products. Thus the t-BoC pathway is favored in future modification of silicon surfaces.
3.6 References

Chapter 4: Conclusion

In this thesis, the vapor pressures of three different ionic liquids samples: 
tetraoctylammonium bis (2-ethyl hexyl) sulfosuccinate ([N8888][AOT]), 1-butyl-3- 
methylimidazolium bis(trifluoromethylsulfonyl)imide ([C4C1Im][NTf2]), and 1,3-bis(3- 
methylimidazolium-yl) propane bis(trifluoromethylsulfonyl)imide ([C3(C1Im)2][NTf2]2) 
are measured using a Knudsen effusion apparatus. The method is calibrated by 
matching the measured benzophenone vapor pressures with literature values, and 
making adjustment to the hole area of the sample cell. Vapor pressure data of ionic 
liquids are plotted and enthalpies of vaporization are obtained.

This thesis also demonstrates two strategies of attaching organic molecules to 
Si(100) surfaces via multi-step modifications. The first strategy includes chlorination of 
H-terminated Si(100) surface, followed by amine substitution and attachment of organic 
molecule. The second strategy includes attachment of t-BoC-protected 11-amino-1-
undecene to the H-terminated Si(100) surface, followed by t-BoC removal and 
attachment of organic molecule.

The synthesized silicon surfaces are examined by X-ray photoelectron 
spectroscopy (XPS). Both qualitative and quantitative analyses are conducted based on 
the spectra obtained and the results indicate organic molecules are attached to the 
silicon surfaces.

Future studies for the attachment of organic functional group to silicon surface 
involve two parts. The first part is to characterize the modified silicon surface with
additional surface techniques reviewed in chapter 1.5. In addition to X-ray photoelectron spectroscopy, these techniques complement the understanding of the modified surface. In particular, the percentage of organic functional group coverage of the surface, the distribution of organic functional group on the silicon surface and the stability of the attached organic functional group are critical pieces of information needed to assess the potential application as a gold ion detector.

The second part for further study aims at the engineering aspect of the modified silicon surface. The main focus is how to create a suitable interface to transfer chemical information from the organic functional group into an electric signal via the silicon surface intermediate, which can then be further interpreted.
VITA

Yuan Li was born in February, 1987 in Wuhan, China, where he finished his elementary, middle and high school degree. He took the national college entrance exam in 2005 and chose to stay in his hometown for undergraduate study at Huazhong University of Science and Technology. He obtained a bachelor’s degree in applied chemistry in June, 2009.

During a visit to Mexico and Canada in summer 2005, he obtained his first image of the United States, a vast land seen onboard a flight from Toronto to Mexico City and beautiful scenery overlooked from the other side of the Niagara Falls. Three years later, when it was the time to decide, he chose to leave his hometown and start a new adventure in the States. He came to Columbia, Missouri, a beautiful college town in August, 2009 and received a Ph.D. degree in chemistry from University of Missouri in 2015.

He is somewhat a well-organized person and good at making all kinds of arrangements. His friends always rely on him for making travel plans (He loves travel too). He is also fond of keeping a record of everything, like experimental data, car service receipts and his lifetime flight log. He has traveled to 24 countries and flown over eight hundred thousand miles by the time this dissertation was finished; 806,035 miles to be exact.