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USING TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY TO
INVESTIGATE BEHAVIOR OF VAPOR-DEPOSITED METAL ON ALKANETHIOL
SELF-ASSEMBLED MONOLAYERS

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ABSTRACT

Metal behavior on alkanethiol self-assembled monolayers (SAMs) has been studied for more than ten years. In the beginning, this system was regarded as an idealized model for understanding the metal/polymer interfaces. In recent years, molecular electronics has developed rapidly. Electronic properties of these devices using a number of functional molecules have been characterized using metal substrate/organic thin film/metal top contact sandwich structures. Therefore, the study of metal/SAM interfaces is of great importance. Our group has employed time-of-flight secondary ion mass spectrometry (ToF-SIMS) to characterize the SAM/top metal contact for many years, and it has proven to be a very powerful technique. Analysis of the mass spectra yields direct information about chemical reactions, metal penetration, and metal nucleation.

In this thesis, ToF-SIMS is applied to study the behavior of K, Au and Ti atoms on several alkanethiol SAMs. Au and Ti are the most commonly used contact metals in molecular electronic studies. The structure of the SAM/Ti interfaces and SAM/Au interfaces are important for measurements of electronic properties of functional molecules. K is an active metal and may be a potential reducing reagent to modify the surface of alkanethiol SAMs. It is also of interest to compare the difference between the chemical activity of K atoms on organic surfaces to that found in organic solvents.

In Chapter 2, the K behavior on C_{15}CH_{3}, (-S(CH_{2})_{15}CH_{3}), C_{15}CO_{2}H, C_{15}CO_{2}CH_{3}, C_{16}OH, and C_{16}OCH_{3} SAMs is investigated. It is found that K atoms react with -CO_{2}H, -CO_{2}CH_{3} and OH groups, forming -CO_{2}K or OK. The K atoms only form complexes
with OCH₃ groups, whereas no chemical reaction is observed on the -CH₃ surface. The activity of these organic functional groups can be ranked as CO₂H > CO₂CH₃ > OH > OCH₃ > CH₃. Most K atoms remain at the vacuum interface with very weak penetration through the organic layer in the CO₂CH₃, CO₂H, OH and OCH₃ systems. At the same time, no chemical interaction between K and the (CH₂)n chain is found, indicating that K dose not alter the basic structure of alkanethiol SAMs.

In Chapter 3, the relationship between metal penetration and inter-molecular interactions is studied via the Au/SAM system. It is found that weak inter-molecular interactions lead to high penetration, and strong inter-molecular interactions lead to low penetration. For example, Au atoms continuously penetrate through C₁₅CH₃ and C₁₅CO₂CH₃ films, forming smooth buried layers under organic thin films. Au atoms penetrate through the CO₂H film, but form clusters due to H-bonding between CO₂H groups. The K modified CO₂CH₃ or CO₂H films are found to prevent Au atoms from leaking through the film. Apparently, the ionic interactions between adjacent film molecules block Au penetration while van der Waals forces and H-bonds do not. Thus, metal penetration can be controlled by adjusting inter-molecular interactions.

In Chapter 4, SAM/Ti top contact interfaces are investigated. Ti/organic functional group interactions can be ranked as Ti/CO₂H > Ti/CO₂CH₃ > Ti/CH₃. Vapor deposited Ti atoms are so active that they damage all surface organic functional groups and the (CH₂)n chain. At the same time, penetration of Ti atoms through the SAMs is weak. The Ti growth on active surfaces prefers a layer-by-layer mode, but the Ti growth on inactive surfaces prefers an island-enlargement process.
The temperature effect on metal penetration through the SAMs is studied in Chapter 5. Decreasing sample temperature is found to reduce metal penetration. However, at low temperature, H$_2$O molecules can be condensed on the sample surface. The effect of H$_2$O molecules on the structure of metal overlayers is not clear.

In this thesis, ToF-SIMS shows its unique ability to acquire information about chemical reactions between metal atoms and surface organic functional groups, penetration of metal atoms through the SAMs, growth modes of metal overlayers on top of the SAMs, and damage to organic molecules. All of these processes which are crucial for understanding the structure of SAM/top metal contact interfaces. It is found that the appearance of new characteristic peaks and the disappearance of initial peaks may indicate chemical reactions or damage of organic molecules. The relationship between metal dose and intensity of surface organic functional group-related peaks may suggest information about penetration or cluster-formation. At the same time, metal overlayers on the SAMs affect the intensities of SIMS signals. Removing the metal overlayers by chemical etching and then characterizing samples again is a complementary method that can supply useful information.
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Chapter 1

Introduction

1.1 SAM on Au substrates

1.1.1 History

In 1983, Nuzzo and Allara reported alkanethiol self-assembled monolayers (SAM) on gold substrates. Since that time, many papers have focused on the study of the properties of alkanethiol SAMs, and a number of excellent reviews have been published. Characteristic of alkanethiol SAMs includes ordered and compact structure, simple preparation, and good stability in ambient conditions. So far, the alkanethiol SAMs have been one of most commonly used model systems for the study of organic thin films.

1.1.2 Preparation

Metallic gold is chosen as a substrate due to two reasons: one is that Au substrates are easy to prepare; the other is that Au is inert so that contamination and oxidation of the Au surface under ambient environment is slow. The later point is very important to form high-quality SAMs. Although many methods have been reported for preparation of Au substrates, the most useful one is physically vapor-deposited Au films on flat Si or glass substrates. Generally, to enhance adherence of Au on the
substrates, a thin layer of Cr or Ti (several nm thick) is pre-deposited before Au deposition⁶. The surface of this substrate is mainly Au(111) facets. This substrate is suitable for most testing and applications. At the same time, the substrate can be stored in ambient for extended period and only simple chemical cleaning is required before use. Under some special experiments, other preparation methods are applied. For example, in scanning probe microscope experiments, atomically flat substrates are needed. Two kinds of methods are commonly used: one is single crystal Au prepared by heating and annealing metal Au wires into small balls; the other is peeled Au films which are prepared by vapor-depositing Au on freshly-cleaved mica sheets. Both methods can supply a relatively large area of atomically flat Au(111) surfaces.

The general procedure to prepare SAMs is to insert Au substrates into alcohol solutions of the corresponding sulfide compounds. After a certain time, the samples are taken out of the solution and dried by flowing nitrogen gas. Many other solvents, such as CH₃OH or iso-propanol, may be used. Although the structures of the SAMs prepared from disulfide compounds are similar to those from sulfide compounds, disulfides are rarely used because the solubility of disulfides is not good. Adsorption of gas phase sulfide compounds is also applied to prepare SAMs, especially in vacuum systems. But at least two disadvantages for this method exist: one is that only small-molecule sulfides have enough vapor pressure, the other is that a dense and compact structure of molecules on Au is difficult to reach due to the nature of adsorption dynamics.
1.1.3 Structure of Alkanethiol SAMs on the Au(111) surface

A typical sulfide molecule is HS(CH$_2$)$_n$X (where X is the organic functional group, such as -CH$_3$, -CO$_2$H, -CO$_2$CH$_3$, -OH, -OCH$_3$, -CONH$_2$, -SH, -CN). This kind of molecule shares similar structure, a head group HS-, a (CH$_2$)$_n$ chain, and a tail group X. -SH groups can chemically interact with the Au surface, forming a Au-S bond. The molecules, then “stand” on the Au substrates$^{3-6}$. The S atoms bind to the 3-fold hollows of the gold lattice ($\sqrt{3} \times \sqrt{3}$ R30°). Because the distance between two adjacent Au atoms on the Au(111) surface is about 0.288 nm, the spacing between two adjacent S atoms is about 0.499 nm (the occupied area of an alkanethiol molecule is about 0.217 nm$^2$). This value is about 3 times the van der Waals diameter of a S atom, so S-S interactions are weak in SAMs. At the same time, this value is also larger than the distance of closest packed alkyl chains (0.424 nm), such that the (CH$_2$)$_n$ chains have to tilt to maximize chain-chain attractive interactions. The tilt angle is determined to be ~27°$^{3-6}$. Finally, the molecules form an ordered and compact structure, and the tail groups are exposed on the surface. Figure 1-1 shows the distribution of S atoms on the Au(111) surface, and Figure 1-2 shows a schematic illustration of an n-alkanethiol SAM.

1.1.4 Applications.

Because of their unique structure and good stability in an ambient environment, alkanethiol SAMs have many applications$^{3-6}$. All these applications can be roughly
Figure 1-1. Schematic illustration of the arrangement of S-atoms on Au(111) lattice when maximum coverage thiolates is attained. The arrangement shown is a (√3×√3)R30° structure where the sulfur atoms (gray balls) are positioned in the 3-fold hollows of the gold lattice (orange balls, α = 2.88Å). The distance between adjacent S atoms is about 0.499 nm.
Figure 1-2. Schematic illustration of the alkanethiol SAMs on gold substrates with a (111) surface. The anatomy and characteristics of the SAM are labeled. (Copied from reference 6)
divided into three main categories. The first category is utilizing the \((\text{CH}_2)_n\) chain as a spacing layer. For example, they can be used as etching resists since their compact structure is not permeable to small molecules such as \(\text{H}_2\text{O}\) and other ions\(^7\). Additionally, the conductance of the \((\text{CH}_2)_n\) chain is poor, so they may be applied as ultra-thin barriers to block electron transport\(^8\). The second category utilizes the surface properties (physical or chemical) of organic functional groups to immobilize interesting objectives. For example, patterned SAMs with hydrophobic and hydrophilic intervals are prepared, and cells are found to attach only onto the hydrophobic areas\(^9\). Additionally, bio-active molecules can be immobilized on SAM surfaces via chemical bonds\(^10\). The third category is modifying metal or metal particle surfaces to give them special surface properties. For example, after SAM modification, Au nanoparticles can form a 3-d crystal\(^11\).

### 1.2 Molecular electronics

#### 1.2.1 History.

Since Aviram and Ratner reported the concept of a molecular rectifier in 1974,\(^12\) molecular electronics research has flourished. Molecular electronics can be defined as “the study of molecular properties that may lead to signal processing”.\(^13\) A relatively wide definition is “technology utilizing single molecule, small group of molecules, carbon nanotubes, or nanoscale metallic or semiconductor wires to perform electronic functions”.\(^14\)
In 1965, Gordon Moore, future chairman and chief executive of Intel stated that at the time that the number of transistors packed into an integrated circuit had doubled every year since the technology's inception four years earlier. In 1975 he revised this so as to occur every two years, and later to 18 months. This prediction is called “Moore’s Law”. Apparently, the trend cannot continue indefinitely with current lithographic techniques, and a limit can be seen in ten to fifteen years. The present semiconductor industry is based on silicon chips. With the density of transistors increasing, the thickness of Si wires in chips becomes thinner and thinner. Thin wire leads to high resistance and high power consumption per unit area. Subsequent heat generation results in many serious problems, such as oxidation of the Si wires or decomposition of supporting materials. Therefore, some new technologies should be invented to overcome this physical limitation of Si chips. The purpose of molecular electronics is to utilize small functional molecules to substitute for traditional Si circuits, thus greatly reducing the size and power consumption.

1.2.2 Representative molecular devices.

So far, many functional molecules have been designed, synthesized and tested. These molecules can be divided into four major categories: molecular rectifiers, switches, wires, and storage devices. However, all these devices are in early development stages and there is still a very long way to go from lab to industry.

A molecular rectifier has a donor-spacer-acceptor structure. It would behave as a diode when placed between two electrodes with potential difference: electrons can
easily flow from the cathode to the acceptor and from the donor to the anode, followed by electrons tunneling from acceptor to the donor. Thus a single-direction conductivity occurs. Since Aviram and Ratner presented this concept in 1974\textsuperscript{12}, a number of molecules have been designed, synthesized and tested. A representative example is the work of Metzger and co-workers\textsuperscript{24}. They synthesized a series of molecules with the C\textsubscript{16}H\textsubscript{33}-acceptor-spacer-donor structure and utilized Langmuir-Blodgett (LB) techniques to immobilize them on metal substrates. With a top metal contact, they find this structure exhibits a very clear rectifying effect.

The molecular switches are used to control current on or off. There are many examples of proposed molecular and atomic switches that operate with different mechanisms\textsuperscript{14,17}. An example is the carbon nanotube field effect transistor\textsuperscript{28}. The device consists of a semiconducting tube positioned across two Pt electrodes on a SiO\textsubscript{2} substrate with doped Si as the back gate. It is found that the conductivity of the carbon nanotube can be controlled by the gate voltage.

The connections between molecular components are important for wiring them as real devices. Molecular wires can serve as these connections. Most research in this area focuses on linear, conjugated molecules. Tour, Weiss, Allara and coworkers have contributed extensively in this field\textsuperscript{19,23}.

In computational architecture, data is stored in a bit-wise manner - the smallest part of data is either 0 or 1. In a molecular system, there are many ways to realize this, such as charge storage, conformational or positional shifting, and physical transformation\textsuperscript{14}. For example, hysteresis behavior is a useful property for information storage applications\textsuperscript{29}.
1.2.3 Testing methods.

To test electronic functions of molecular devices, functional molecules should be connected to outer circuits (generally, metal wires), and the fabrication of the metal-molecular junction is a problem. A number of techniques have been developed, and two of them are relatively common\textsuperscript{23,26,27}: one is utilizing STM/AFM to test objective molecules immobilized on a flat metal or semiconductor substrate; the other is fabricating metal substrate/organic thin film/top metal contact sandwich structure.

In STM/AFM measurements, objective molecules are immobilized on flat substrates by a self-assembly technique. For example, one end of the objective molecule can be modified by a -SH group, so that it can stand on Au substrates via a Au-S bond. The objective molecules can be inserted into a C\textsubscript{n} SAM matrix or they can directly form SAMs on the Au substrates. However, for the later situation it is a little difficult to determine how many molecules are under the tip of STM/AFM.

To prepare metal/organic thin film/metal sandwiches, the first step is to immobilize the organic thin film on the metal substrates via self-assembly or LB technique. Then the top metal contact can be vapor-evaporated on the films. To avoid possible defects or shorts, the effective area should be as small as possible. Therefore, the cross-bar technique\textsuperscript{30} and the nanopore technique\textsuperscript{31} are developed to minimize the effective areas.

Many other techniques, such as Hg drop junctions, break junctions, and cross-wires, have been reported\textsuperscript{23,26,27}. However, currently there is not a mature and effective
method to wire single molecules up to be a functional device. Therefore, more nano-fabrication techniques need to be developed to overcome this obstacle.

1.3 Characterization of Metal/SAM interfaces

1.3.1 Why this system is so interesting?

The behavior of vapor-evaporated metal atoms on alkanethiol SAMs has been studied for more than a decade. Initially, this system was regarded as a model system to elucidate metal/polymer interfaces. Typically, a polymer surface is not composed of only one kind of organic functional group, but several different kinds of groups. Thus, directly studying metal/polymer interfaces is quite complex. Alkanethiol SAMs on Au substrates have very ordered structures, with only one kind of organic functional group at the vacuum interface, so they are very good model systems to elucidate metal behavior on polymer surfaces.

In recent years, molecular electronics has developed quite quickly. The purpose of molecular electronics is trying to prepare functional organic molecules and using them to substitute present silicon chips, greatly reducing the size and power consumption. So far, many affords have been reported. One of the most commonly used structures to measure the electric properties of these functional organic molecules is metal substrate/SAM or LB film/top contact metal sandwiches. Vapor-evaporating metals on top of the organic thin films is a major way to prepare top metal contact. Apparently the structure of top metal/organic thin film interfaces affects the measurement
results. Therefore, the characterization of the top metal/organic thin film interfaces is necessary.

1.3.2 Techniques used to investigate of Metal/SAM interfaces.

The following questions are important at the metal/SAM interfaces: (1) are there chemical reactions between the surface organic functional groups and metal atoms; (2) do metal atoms stay on top of the SAM or penetrate through the SAM; (3) if metal atoms stay on top of the SAM, how about the nucleation and growth modes; (4) if metal atoms penetrate through the SAM, they form smooth layer or clusters or filament or mushroom-like structure; (5) if chemical reactions occur on surface organic functional groups, are \((\text{CH}_2)_n\) chains damaged or not. To answer these questions, a number of techniques are applied to investigate the top metal contact/SAM interface, including X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), reflection absorption infrared spectrometry (RAIRS), secondary ion mass spectrometry (SIMS), scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

XPS provides information about elements and their chemical states. For example, before Ti is deposited on \(\text{CO}_2\text{CH}_3\) surface, three kinds of carbon atoms are found, and they are assigned as \((*\text{CH}_2)_n\), \(*\text{CO}_2\text{CH}_3\), \(*\text{CO}_2*\text{CH}_3\). After Ti deposition, the later two carbon signals disappear and the \((*\text{CH}_2)_n\) signal greatly decreases. At the same time, a new peak assigned as Ti-*C appears. All data suggest that Ti damages \(\text{CO}_2\text{CH}_3\) groups as well as \((\text{CH}_2)_n\) chain, forming Ti,\(\text{C}_y\) complexes.
ISS provides information of elements and their depth distribution. For example, at room temperature, after 1.0 nm of Ag is deposited on S(CH$_2$)$_{17}$CH$_3$ SAM, no Ag signal is found at the surface. With sputtering, Ag signal gradually appears, suggesting that Ag atoms penetrate through the film and arrive Au/S interface. However, if Ag is deposited on a S(CH$_2$)$_{17}$CH$_3$ sample at 90K, Ag signal appears at the very beginning of the sputtering, indicating that Ag atoms stay on top of the film surface$^{35,58,59}$.

IR can provide information about organic functional groups and orientation of the molecules. For example, when 1.0 nm of K is deposited on CO$_2$CH$_3$ surface, CH$_3$ and C=O bond-related signals disappear, and two new peaks assigned as CO$_2^-$ symmetric and asymmetric modes appear, implying that CO$_2$CH$_3$ groups react with K atoms to form CO$_2^-$K$^+$. At the same time, CH$_2$ stretch peaks move to high frequencies and become slightly wider, indicating that the (CH$_2$)$_n$ chains are slightly disordered$^{34}$.

STM and AFM provide topography information and electric-conductive properties. For example, Au is deposited on C$_n$ SAMs and STM is used to study these systems. Most of Au atoms form smooth layers under the organic thin film, but a number of them form clusters on top of the film. The evidence for surface Au clusters is the existence of the Coulomb blockade and Coulomb staircase in these systems$^{64}$.

Our group has utilized time-of-flight secondary ion mass spectrometry (ToF-SIMS) to examine the behavior of vapor-deposited Al, Au, Ag, Cu, K, Ti and other metals on a number of alkanethiol films$^{52-57,60-62}$. Detailed structural information of top metal contact/SAM interfaces has been obtained using ToF-SIMS. For example, Al/SAM system has been examined$^{55-57}$, and it is found that the appearance of Al/surface organic functional group clusters is an indicator of Al atoms that deposit on the surface of the
SAM at the vacuum interface. The observation of AlSH$_2^+$ ions is an indicator for Al penetrating through the organic thin film to the Au/S interface. If both kinds of ions are detected, we believe that some of Al atoms penetrate through the film, and some of the Al atoms stay at the vacuum interface. Disappearance of initial peaks and appearance of new peaks may be indicative of chemical reactions. When K was deposited on S(CH$_2$)$_{15}$CO$_2$CH$_3$ and S(CH$_2$)$_{15}$CO$_2$H films, the disappearance of molecular peaks with the increase of the S(CH$_2$)$_{15}$CO$_2$K$^+$ peak imply that CO$_2$CH$_3$ and CO$_2$H groups react with K atoms to form CO$_2$K groups$^{62,67}$. Additionally, the intensity trend of characteristic peaks as a function of metal dose also supplies useful information. For example, when K is simultaneously evaporated on CH$_3$, CO$_2$CH$_3$ and CO$_2$H-terminated films, the K$^+$ signal on the CH$_3$ film is much weaker than those on the other two films, suggesting that the sticking coefficient of K atoms on the CH$_3$ surface is much lower than that on CO$_2$H and CO$_2$CH$_3$ surfaces$^{62,67}$. Furthermore, ToF-SIMS has a very shallow information depth, generally 1-2 atomic layers. Therefore, it is possible to determine the modes of metal growth by checking the dose-intensity relationship. For example, it is easy to distinguish layer-by-layer growth and 3-d cluster formation by comparing the decreasing rate of original molecular ions from the substrate$^{68}$.

Single technique detection only provides limited information. For example, SIMS can provide molecular information but no topography or electric-conductive information. STM/AFM can provide both topography and electric-conductive information, but no chemical information. To understand top metal contact/SAM interfaces comprehensively, multi-technique investigation is needed. A collaboration has been applied between our
research group and the Allara group at the Penn State University. A number of interesting results have been discovered\textsuperscript{52-57,60-62} and more efforts are under way.

1.3.3 Representative scenarios of Metal/SAM interfaces.

Four representative scenarios of metal/SAM interfaces are known. Figure 1-3A shows that metal atoms can penetrate through the SAMs and form smooth inter-layers at the Au/S interface. This situation results from weak interactions between metal atoms and surface organic functional groups as well as weak intermolecular interactions (for example, Au or Ag on the CH\textsubscript{3} surface)\textsuperscript{35,63,64,69,70}. Figure 1-3B shows a partial penetration mode, in which a fraction of metal atoms penetrate through the SAMs and others stay on top of the film. The chance for appearance of filaments and mushroom-like structure is high. This situation results from relative weak interaction between metal atoms and surface organic functional groups (Al on OCH\textsubscript{3})\textsuperscript{55}, or relative strong intermolecular interactions in SAMs (Au on CO\textsubscript{2}H)\textsuperscript{71}. Figure 1-3C shows that metal atoms stay at the vacuum interface with weak penetration and form relative smooth overlayers. This situation results from strong interactions between metal atoms and organic functional groups (Al or K on CO\textsubscript{2}CH\textsubscript{3} surface)\textsuperscript{57,62,67}. However, if super-active metal atoms are deposited on the SAMs, although most metal atoms stay on top of the films, both the surface organic functional groups and the (CH\textsubscript{2})\textsubscript{n} chain are damaged (Figure 1-3D, Ti/Cr on CO\textsubscript{2}CH\textsubscript{3} surface)\textsuperscript{39,40,68,72}. 
Figure 1-3. Schematic illustration of metal behavior on alkanethiol SAMs. (A), smooth interlayer between Au substrate and alkanethiol film; (B), partial penetration; (C), smooth overlayer with very weak penetration; (D), decomposition of organic molecules. The blue balls represent metal atoms.
1.4 The purpose of this thesis

In this thesis, K on CH₃, CO₂H, CO₂CH₃, OH, and OCH₃-terminated SAMs, Au and Ti on CH₃, CO₂H, CO₂CH₃, and CO₂K-terminated SAMs are studied by ToF-SIMS.

K is a useful reduction reagent in organic synthesis. One purpose of our research is to test reactivity of surface organic functional groups and compare the results with traditional organic reactions. At the same time, we want to know if K is a safe reagent to modify surface organic functional groups of alkanethiol SAMs.

Au and Ti are the most commonly used contact metals in preparation of metal/organic thin film/metal sandwich structures. Clearly understanding the structure of Au/SAM and Ti/SAM interfaces is necessary. Unfortunately, Au is found to penetrate through alkanethiol SAMs easily at room temperature due to weak intermolecular interactions and weak interactions between Au atoms and surface organic functional groups. In this thesis, the relationship between Au penetration and intensity of intermolecular interactions is investigated. At the same time, we try to block Au penetration by introducing strong ionic interactions between organic molecules. Ti is found to damage organic functional groups as well as (CH₂)ₙ chains, but previous data are not enough to clearly describe Ti/SAM interfaces. Therefore, more data are needed to clarify some important details.

Based on SIMS data, schematic models are established to describe metal behavior on SAMs. Chemical reactions between metal atoms and surface organic functional groups, penetration of metal atoms, formation and distribution of metal clusters, growth
of metal overlayers on top of the organic thin films, damage of \((\text{CH}_2)_n\) chains are all investigated in my research. The influencing factors on behavior of metal atoms are also discussed.
1.5 References:


(67) Zhu, Z.; Allara, D. L.; Winograd, N. paper In preparation


Chapter 2

**K on CO\textsubscript{2}H, CO\textsubscript{2}CH\textsubscript{3}, OH, OCH\textsubscript{3} and CH\textsubscript{3}-Terminated SAMs**

### 2.1 Introduction

Alkanethiol self-assembled monolayer (SAM) was first reported by Nuzzo and Allara in 1983\textsuperscript{1}. One of the most distinguished properties of alkanethiol SAMs is that only one kind of organic functional group is exposed at the vacuum interface. At the same time, the preparation of SAMs is relatively simple. Thus, alkanethiol SAMs have been one of the most widely used substrates in scientific research\textsuperscript{2,3}. The structure of alkanethiol SAMs on Au substrates has been described in many papers\textsuperscript{4-6}. Briefly, alkanethiol molecules are anchored on a Au substrate via a Au-S chemical bond. The van der Waals interactions between alkanethiol molecules make them closely packed, forming very a regular structure. The strong Au-S interaction and compact structure of the film make alkanethiol SAMs stable under some severe circumstances.

K is an active metal and reactions between K and many organic functional groups have been described in many organic chemistry textbooks. Additionally, K is a very important reducing reagent in organic synthesis. For example, in the famous Birch reduction, K reduces benzene into 1,4-cyclohexadiene in liquid ammonia. During the last thirty years, K is found to be a very good reducing reagent in a number of sophisticated organic reactions\textsuperscript{7-13}. 
In this work, we studied K behavior on several alkanethiol SAMs with different surface organic functional groups. One of the purposes is to compare chemical reactions between K atoms and organic functional groups in normal organic reactions and surface reactions. In addition, chemical modification is an important method to change the surface properties (for example, wetting or chemical reactivity) of SAMs. K may be used as the reducing reagent for modification of surfaces. For example, depositing K atoms onto CO$_2$H or CO$_2$CH$_3$ surfaces may be a good way to prepare a clean CO$_2$K surface under vacuum. The CO$_2$K surface is interesting because it may be applied as a buffer layer to block the penetration of metal atoms through alkanethiol SAMs. Vapor-depositing metals on top of alkanethiol SAMs is a common way to prepare Au/SAM/top metal contact sandwich structures, which have been used in the detection of electronic properties of some molecular electronic devices. However, vapor metal atoms may penetrate through the SAMs via some temporary vacancies, which are generated by thermal energy. If the interactions between film molecules are dominated by strong ionic interactions, which are much stronger than thermal energy at room temperature, such temporary vacancies cannot be formed and metal penetration should be blocked. Therefore, studying the K behavior on the alkanethiol SAMs is necessary.

The main technique used in this work is time-of-flight secondary ion mass spectroscopy (ToF-SIMS). ToF-SIMS has proven to be a powerful technique for the study of the interaction of metal atoms with organic thin film surfaces. Analysis of the mass spectra yields direct information about chemical reactions, metal penetration and metal nucleation. For example, the behavior of thermally evaporated Al atoms on S(CH$_2$)$_{15}$X (X = -CO$_2$H, -CO$_2$CH$_3$, -CH$_2$OH, -CH$_2$OCH$_3$ and -CH$_3$) SAMs has been
studied using ToF-SIMS\textsuperscript{16,24,25}. It is found that the presence of Al-surface organic functional group cluster ions indicates that at least a fraction of deposited Al atoms remain at the vacuum interface and the detection of AlSH\textsubscript{2}\textsuperscript{+} cluster ions is an indicator of metal penetration. Additionally, the appearance of new characteristic peaks suggests some special chemical reactions. For example, CO\textsubscript{2}Al\textsuperscript{+} ions are detected after Al is deposited on the CO\textsubscript{2}CH\textsubscript{3} surface, indicating that CO\textsubscript{2}CH\textsubscript{3} groups react with Al atoms to form CO\textsubscript{2}\textsuperscript{-} moieties. The formation of metal clusters can be tracked from intensity trend of molecular peaks. For example, Au\textsubscript{2}M\textsuperscript{-} and AuM\textsubscript{2}\textsuperscript{-} peaks (M = S(CH\textsubscript{2})\textsubscript{15}X) decrease very fast after low dose of Al (0.2 nm) on the CO\textsubscript{2}H, CO\textsubscript{2}CH\textsubscript{3} and OH surfaces. On the contrary, these peaks are still very strong even after 0.4 nm of Al on the OCH\textsubscript{3} and CH\textsubscript{3} surfaces. The above results show that Al forms smooth layers on the CO\textsubscript{2}H, CO\textsubscript{2}CH\textsubscript{3} and OH surfaces, but forms 3-dimensional clusters in the OCH\textsubscript{3} and CH\textsubscript{3} systems.

Although ToF-SIMS can supply a lot of chemical and structural information, it has limitations. For example, it cannot supply the information about the order degree of the (CH\textsubscript{2})\textsubscript{n} backbone in the system. Reflection IR spectroscopy was used in our studies. IR spectra can supply not only the information about the order degree of (CH\textsubscript{2})\textsubscript{n} backbone, but also information about chemical reactions. Therefore, IR spectroscopy can reinforce the conclusions made from the SIMS spectra.

In this paper, ToF-SIMS and IR are applied to study the K behavior on S(CH\textsubscript{2})\textsubscript{15}X (X = -CO\textsubscript{2}H, -CO\textsubscript{2}CH\textsubscript{3}, -CH\textsubscript{2}OH, -CH\textsubscript{2}OCH\textsubscript{3} and -CH\textsubscript{3}) SAMs on Au substrates. It is found that K atoms react with CO\textsubscript{2}CH\textsubscript{3} and CO\textsubscript{2}H groups to form a CO\textsubscript{2}K surface. The OH groups can react with K atoms, forming OK, but the reaction is not complete at a dose of 1.0 nm of K. The OCH\textsubscript{3} groups only form complexes with K atoms, and no
detectable chemical reactions are observed. At the same time, the backbone of the film molecules (the -(CH\(_2\)_n- chain) is free of chemical reactions, with very weak K penetration through any of the above four films. Additionally, no chemical reactions are observed in the CH\(_3\) system and the sticking coefficient of K atoms on the CH\(_3\) surface is quite low. The reactions between K atoms and organic functional groups at the vacuum interface are in agreement with reactions in bulk conditions. The reactivity of the organic functional groups can be ranked as CO\(_2\)H > CO\(_2\)CH\(_3\) > OH > OCH\(_3\) > CH\(_3\).

2.2 Experimental

2.2.1 SAM Preparation

The preparation and characterization of the S(CH\(_2\))\(_{15}\)CO\(_2\)H, S(CH\(_2\))\(_{15}\)CO\(_2\)CH\(_3\), S(CH\(_2\))\(_{15}\)CH\(_2\)OH, S(CH\(_2\))\(_{15}\)CH\(_2\)OCH\(_3\), and S(CH\(_2\))\(_{15}\)CH\(_3\) SAMs used in this study have been described in detail previously\(^{16,24,25}\). Briefly, Cr (~10 nm) and Au (~200 nm) were thermally deposited sequentially onto clean Si(001) wafers. The films were prepared by immersing the Au substrates into 1.0 mM solutions of the relevant alkanethiol molecules in absolute ethanol for ~2 days at ambient temperature. Before the samples were put into the vacuum, they were thoroughly rinsed by absolute alcohol and dried by flowing pure nitrogen gas. The films were characterized with single wavelength ellipsometry, infrared spectroscopy, and contact angle measurements to ensure dense packing and clean surfaces. For convenience, in this paper, the above five films are referred to as CO\(_2\)H, CO\(_2\)CH\(_3\), OH, OCH\(_3\), and CH\(_3\) films, respectively.
2 2.2. Time-of-Flight Secondary Ion Mass Spectrometry

The ToF-SIMS analyses were performed on a custom designed instrument, as described previously\textsuperscript{26}. Briefly, the instrument consists of a loadlock, a metal deposition chamber, a preparation chamber, and a primary analysis chamber, each separated by a gate valve. 15 keV Ga\textsuperscript{+} ions were used as primary ions. The ions were contained in a 100 nm diameter beam that was rastered over a $300 \times 300 \ \mu \text{m}^2$ area during data acquisition. All spectra were acquired using a total ion dose of less than $10^{11}$ ions/cm\textsuperscript{2}. Relative peak intensities are reproducible to within $\pm 8\%$ from both sample-to-sample and scan to scan. In all measurements, the pressure in the analysis chamber is about $2.0 \times 10^{-10}$ torr.

2.2.3 K Deposition

Atomic K was deposited on top of the samples in the metal deposition chamber using a dispenser (SAES getters), which was located about 50 cm vertically above the SAM samples, at a rate of 0.001 nm/s. Metal thickness was monitored by a quartz crystal microbalance (Maxtek TM400 controller, 6MHz Sycon crystal head), which was located at the side of the samples.

In our study, five film samples (CO\textsubscript{2}H, CO\textsubscript{2}CH\textsubscript{3}, OH, OCH\textsubscript{3}, and CH\textsubscript{3}) were immobilized on a sample block and were put into vacuum. SIMS spectra of freshly prepared monolayers were taken firstly, and then the samples were transferred under vacuum to the metal deposition chamber, where K atoms were deposited on the samples. After K deposition, the samples were transferred back to the analysis chamber to acquire
SIMS spectra. Each transfer time was about 4-6 min. The pressure of the deposition chamber before K deposition was about $1.2 \times 10^{-9}$ Torr; and was $<2 \times 10^{-7}$ Torr during K deposition. After SIMS analysis, the samples were redosed with additional K. This process was repeated several times until a total K dose reaches about 1.0 nm. Note that one monolayer of K atoms is about 0.4 nm thick and 0.34 nm K is enough for one K atom per organic functional group for all films. In another experiment, 1.20 nm of K was directly deposited on the samples. After SIMS measurement, the samples were then removed from vacuum and rinsed with ultra-pure water (18.2 MΩ·cm, Milli-Q system, Millipore, Burlington, MA). After drying, they were put back into the analysis chamber.

### 2.2.4 Infrared Spectroscopy

The IR instrument has been described elsewhere\textsuperscript{16}. In brief, analyses were performed on a Fourier transform instrument (Mattson Research Series 1000) fitted with custom in-house optics configured externally to the instrument and designed for grazing incidence reflection of samples under vacuum. A liquid nitrogen cooled MCT detector was used with an effective low frequency cutoff of $\sim 750$ cm$^{-1}$. The infrared beam passed through the analysis chamber through a pair of differentially-pumped KBr windows. K deposition rates were controlled to 0.001nm/s. The pressure remained $<3 \times 10^{-7}$ torr during the deposition.
**2.2.5 Sticking Coefficient Determination**

To determine the sticking coefficient of K atoms on different surfaces, QCM experiments were applied. Two QCM heads (both with 6MHz crystals, and ~200 nm Au attached on the crystals via a ~10 nm Cr adhesion layer) were immobilized side-by-side 50 cm under the K source. A hand-controlled shutter was positioned ~2 cm over the QCM heads. Both crystals have a smooth surface and are modified by alkanethiol SAMs. The smooth QCM crystals (Cold Springs R&D, Syracuse, NY) were highly polished on top side, resulting in the QCM SAM surfaces having near identical RMS roughness values to those of the SAMs prepared on silicon substrates. The first crystal acts as the reference, and its surface was modified by S(CH$_2$)$_{15}$CO$_2$CH$_3$ SAM. The CO$_2$CH$_3$ surface was applied as the reference because K/CO$_2$CH$_3$ interactions are strong and the sticking probability of K atoms on this surface should be close to 100%. The surface of the second crystal was modified by the objective SAM. In our experiments, both crystals were simultaneously exposed to vapors. K deposition rates were controlled in the same fashion as those reported earlier for the SIMS and IR experiments.

**2.3 Results and Discussion**

**2.3.1 SIMS spectra of freshly prepared SAMs**

ToF-SIMS spectra of all five films have been described previously$^{16,24,25,27-31}$. All characteristic peaks with m/z < 1000 amu are labeled in our study, and they are consistent
with previously published results. Briefly, for all films, $C_nH_m^\pm$, $S^-$, $SH^-$, $SC_nH_m^\pm$, $Au_n^\pm$, $Au_nS_mH_1^\pm$, $AuC_nH_m^\pm$, $AuSC_nH_m^\pm$ are common peaks. Molecular peaks in positive ion spectra are weak. But in negative ion spectra, many molecular peaks can be observed, such as $HAuM^-$, $Au_2M^-$, $AuM_2^-$ ($M = S(CH_2)_15X$) peaks. The details of these molecular peaks were listed in Table 2-1.

**Table 2-1 Molecular Peaks of the Films**

<table>
<thead>
<tr>
<th>Charge</th>
<th>M</th>
<th>AuM</th>
<th>AuM_2</th>
<th>Au_2M</th>
<th>Au_2M_2</th>
<th>Au_3M</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>−</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>$C_{15}CO_2CH_3$</td>
<td>x</td>
<td>x</td>
<td>√</td>
<td>√</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td>$C_{15}CO_2H$</td>
<td>x</td>
<td>x</td>
<td>√*</td>
<td>√*</td>
<td>x</td>
<td>√*</td>
</tr>
<tr>
<td>$C_{16}OH$</td>
<td>x</td>
<td>x</td>
<td>√</td>
<td>√</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td>$C_{16}OCH_3$</td>
<td>x</td>
<td>√</td>
<td>√*</td>
<td>√</td>
<td>x</td>
<td>√</td>
</tr>
<tr>
<td>$C_{15}CH_3$</td>
<td>x</td>
<td>x</td>
<td>√</td>
<td>√</td>
<td>x</td>
<td>√</td>
</tr>
</tbody>
</table>

x: too weak to be found; √*: found but relative weak; √: moderate to strong.

Besides the molecular peaks, different films have their own characteristic fragment peaks. For example, for $CO_2CH_3$ film, $CH_3^+$, $OCH_3^\pm$, $CO_2CH_3^+$, $C_nH_mO^+$, $O^-$, $OH^-$ peaks are observed; for $CO_2H$ film, $H_3O^+$, $CO_2H^+$, $(CH_2)_nCO_2H^+$, $C_nH_mO^+$, $O^-$, $OH^-$, $C_2OH^-$, $C_nH_mCO_2^-$, $AuS(CH_2)_15^-$ peaks are observed; for $OH$ film, $H_3O^+$, $(CH_2)_nOH^+$, $O^-$, $OH^-$, $C_2OH^-$ peaks are found; and for $OCH_3$ film, $OCH_3^\pm$, $(CH_2)_nOCH_3^+$, $O^-$, $OH^-$ peaks are observed.
**2.3.2 K on CO\(_2\)CH\(_3\) film**

The \(^{39}\text{K}^+\) peak dominates the positive ion spectrum after a K dose of 0.05 nm, and all original peaks greatly decrease (Figure 2-1). Figure 2-2 shows K\(^+\), Au\(^+\) and CO\(_2\)K\(_2^+\) peaks with increasing amounts of K dose. The \(^{39}\text{K}^+\) peak increases with increasing amounts of K, and finally reaches a steady state after 0.63 nm of K (Figure 2-2a). Au\(^+\) ion signal quickly decreases to the noise level after \(\sim0.33\) nm of K (Figure 2-2b). K\(_2\)O\(^+\), K\(_2\)OH\(^+\), CO\(_2\)K\(_2^+\), (CH\(_2\))\(_n\)CO\(_2\)K\(_2^+\) ions are found after K deposition, indicating that CO\(_2\)CH\(_3\) groups react with K atoms to form CO\(_2\)K moieties. Figure 2-2c shows the high-resolution spectra of the CO\(_2\)K\(_2^+\) peak. It is found that this peak increases at the beginning and slightly decreases after 0.63 nm of K. All CO\(_2\)K moiety related ions, for example K\(_2\)O\(^+\), K\(_2\)OH\(^+\), CO\(_2\)K\(_2^+\), (CH\(_2\))\(_n\)CO\(_2\)K\(_2^+\), share this trend. The initial increase of these peaks can be explained by the formation of CO\(_2\)K moieties at the surface, and the final decrease may be attributed to two reasons. One is the decrease of surface work function caused by accumulation of K atoms\(^{32-34}\); the other is the overlayers of K atoms on the CO\(_2\)K layers. These two factors may also lead to the rapid decrease of the intensities of the original positive ion peaks from the CO\(_2\)CH\(_3\) film and the intensity limitation of the \(^{39}\text{K}^+\) signal.

\([\text{S(CH}_2\text{)}_{15}\text{CO}_2\text{K}]^-\) ions (m/z = 325.16 amu) are found after K deposition and continuously increase with K deposition (Figure 2-3a). At the same time, the \([\text{S(CH}_2\text{)}_{15}\text{CO}_2\text{CH}_3]^-\) (m/z = 301.22 amu) peak initially increases with K deposition and then finally decreases to noise level after a dose of 0.83 nm (Figure 2-3b). The data
Figure 2-1. The positive ion spectra of a CO$_2$CH$_3$ film and this sample after 0.05 nm K deposition.
Figure 2-2. K⁺ (a), Au⁺ (b), and CO₂K₂⁺ (c) peaks from the positive ion spectra of the CO₂CH₃ film with increasing amounts of K dose.
Figure 2-3. [S(CH$_2$)$_{15}$CO$_2$K]$^-$ and [S(CH$_2$)$_{15}$CO$_2$CH$_3$]$^-$ peaks from the negative ion spectra of the CO$_2$CH$_3$ film with increasing amounts of K dose.
clearly show that CO$_2$CH$_3$ groups react with K atoms to form CO$_2$K moieties, and after 0.83 nm K deposition, the reaction is complete. The intensity trend of OCH$_3^-$, [HAuS(CH$_2$)$_{15}$CO$_2$CH$_3$]$^-$ and [Au$_2$S(CH$_2$)$_{15}$CO$_2$CH$_3$]$^-$ peaks also support this point (Figure 2-4). Here, the initial increase of the negative ion signals is attributed to the decrease of work function due to accumulation of K atoms.

To fully understand the surface reaction, 1.20 nm K was deposited on a CO$_2$CH$_3$ film, and this sample was rinsed by water thoroughly. Figure 2-5 left shows the negative spectra of a CO$_2$CH$_3$ film, this film after 1.20 nm K deposition and water rinse, and a CO$_2$H film. It is found that the spectrum of the CO$_2$CH$_3$ film after 1.20 nm K deposition and water rinse is very similar to the spectrum of the CO$_2$H film, and the characteristic peaks of the original CO$_2$CH$_3$ film nearly disappear. Additionally, the K$^+$ peak is very weak after the water rinse (Figure 2-5 right). The above data strongly support that 1.20 nm of K reacts with all CO$_2$CH$_3$ groups, forming CO$_2$K moieties; and with a water rinse, the CO$_2$K moieties react with water, forming CO$_2$H groups. Both reactions are rather complete and clean. Additionally, most K atoms disappear after the water rinse, indicating most of the K atoms do not penetrate through the film but stay at the vacuum interface, because if K atoms reach the Au/S interface, the water rinse should not easily remove them due to the compact structure of the film$^{35,36}$. These results prove that K is a safe reagent to modify surface organic functional groups of alkanethiol SAMs.

Figure 2-6 shows the IR spectra of a freshly-prepared CO$_2$CH$_3$ film (a), this film after ~2.0 nm K deposition (b), this sample after K deposition and water rinse (c), and a
Figure 2-4. The intensity trend of OCH$_3^-$, [HAuS(CH$_2$)$_{15}$CO$_2$CH$_3$]$,^-$ and [Au$_2$S(CH$_2$)$_{15}$CO$_2$CH$_3$]$^-$ peaks from negative ion spectra of the CO$_2$CH$_3$ film with increasing amounts of K dose. I$_0$ is the original peak intensity before K deposition, and I is the peak intensity after exposure of a certain amount of K vapor.
Figure 2-5. ToF-SIMS spectra of a CO₂CH₃ film with K deposition and water rinse. Left, negative ion spectra, [Au₂S(CH₂)₁₅CO₂CH₃]⁻ (X = CO₂CH₃, CO₂H) area of a freshly prepared CO₂CH₃ film (a), this sample after 1.2 nm K deposition and water rinse (b), and a CO₂H film (c). Right, positive ion spectra, ⁴¹K⁺ area of a freshly prepared CO₂CH₃ film (a), this sample after 1.2 nm K deposition (b), and this sample after 1.2 nm K deposition and water rinse (c).
Figure 2-6. IRS spectra of a CO$_2$CH$_3$ sample (a), this sample after 2.0 nm K deposition (b), this sample after 2.0 nm K deposition and water rinse (c), and a CO$_2$H sample (d).

For the CO$_2$CH$_3$ sample, 2955, CH$_3$ C-H asym str; 2918, CH$_2$, CH asym str; 2850, CH$_2$, C-H sym str; 1745, C=O str; 1440, CH$_3$ sym def; 1150-1350, chain wags and twists (progression bands); 1207, C-O str; 1178, C-O str. For the K-modified CO$_2$CH$_3$ sample, 1409 and 1428, COO$^-$ sym str; 1575 and 1597, COO$^-$ asym str. For the CO$_2$H sample, 1414 and 1468, CH$_2$, scissors def; 1718, hydrogen-bonded C=O str; 1742, non-hydrogen-bonded C=O str.
freshly-prepared CO$_2$H film (d). Peak assignment has been reported in previous papers$^{16,37}$. All CO$_2$CH$_3$-related peaks, such as CH$_3$ asymmetric stretch (2955 cm$^{-1}$), O-CH$_3$ bend (1440 cm$^{-1}$), C=O stretch (1745 cm$^{-1}$) and C-O stretch (1207, 1178 cm$^{-1}$) disappear after K deposition, suggesting that all CO$_2$CH$_3$ groups react with the K atoms. Two wide peaks appear in the low frequency area and they are assigned as CO$_2^-$ symmetric stretch (1409, 1428 cm$^{-1}$) and CO$_2^-$ asymmetric stretch (1575, 1597 cm$^{-1}$)$^{38}$. The above data strongly suggest that CO$_2^-$K$^+$ moieties form on the vacuum interface. After a water rinse, CO$_2^-$ peaks disappear, and the spectrum is very similar to the spectrum of a CO$_2$H film, suggesting that CO$_2$K moieties become CO$_2$H groups. The above results are consistent with the SIMS results. However, compared with a freshly prepared CO$_2$H sample, 1718 cm$^{-1}$ peak is much stronger for this modification-prepared CO$_2$H film. This peak is assigned as the stretch of hydrogen-bonded C=O bond. The 1742 cm$^{-1}$ peak is corresponding to the non-hydrogen-bonded C=O bond. Therefore, the structure of this K-modification-prepared CO$_2$H film is slightly different from that of a freshly-prepared CO$_2$H film. In a freshly-prepared CO$_2$H film, only about half of the CO$_2$H groups were involved in hydrogen-bonds, but for the modification-prepared CO$_2$H film, the main fraction of CO$_2$H groups are involved in hydrogen-bonds.

After K modification, CH$_2$ stretch (2850, 2918 cm$^{-1}$) peaks move to high frequency (2854, 2926 cm$^{-1}$), and become a little broader (see Table 2-2), indicating the (CH$_2$)$_n$ chain becomes disordered. After water rinse, the CH$_2$ stretch peaks move back (2851, 2920 cm$^{-1}$), but still a little higher than the original frequency, and the peak width is also a little broader, implying that the (CH$_2$)$_n$ chain is not as ordered as that in the original CO$_2$CH$_3$ film. An interesting observation is that the peak width of the CH$_2$
stretch peaks of the modification-prepared CO$_2$H film is thinner than that of the freshly-prepared CO$_2$H film (see Table 2-2), suggesting that the order degree of the (CH$_2$)$_n$ chain in the modification-prepared CO$_2$H film is higher. This point is reasonable because it is corresponding to the observation that more hydrogen bonds exist in the modification-prepared CO$_2$H sample.

Table 2-2. Peak position and width of CH$_2$ symmetric and asymmetric stretch peaks

<table>
<thead>
<tr>
<th></th>
<th>CH$_2$ (sym)</th>
<th></th>
<th>CH$_2$ (asym)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency/cm$^{-1}$</td>
<td>Width/cm$^{-1}$</td>
<td>Frequency/cm$^{-1}$</td>
<td>Width/cm$^{-1}$</td>
</tr>
<tr>
<td>CO$_2$CH$_3$</td>
<td>2850</td>
<td>10</td>
<td>2918</td>
<td>12</td>
</tr>
<tr>
<td>CO$_2$CH$_3$/K</td>
<td>2854</td>
<td>17</td>
<td>2926</td>
<td>23</td>
</tr>
<tr>
<td>CO$_2$CH$_3$/K/H$_2$O</td>
<td>2851</td>
<td>14</td>
<td>2920</td>
<td>17</td>
</tr>
<tr>
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<td>25</td>
</tr>
<tr>
<td>CO$_2$H/K/H$_2$O</td>
<td>2851</td>
<td>14</td>
<td>2920</td>
<td>17</td>
</tr>
</tbody>
</table>

2.3.3 K on CO$_2$H film

The SIMS spectra of a CO$_2$H film after K deposition are very similar to those of the CO$_2$CH$_3$/K system. For example, $^{39}$K$^+$ peak dominates the positive spectra after K deposition. K$_2$O$^+$, K$_2$OH$^+$, CO$_2$K$_2^+$, (CH$_2$)$_n$CO$_2$K$_2^+$ peaks are also found and share the
same trend with those from the CO$_2$CH$_3$/K system. All original positive ion peaks also greatly decrease with K deposition.

[S(CH$_2$)$_{15}$CO$_2$K]$^-$ signal is found and continuously increases with K deposition (Figure 2-7a). At the same time, [S(CH$_2$)$_{15}$CO$_2$H]$^-$ (m/z = 287.21 amu) peak increases with K deposition and then decreases, finally reaches noise level after a dose of about 0.33 nm (Figure 2-7b). This result indicates that 0.33 nm of K is enough to react with all CO$_2$H groups to form CO$_2$K moieties. The intensity trend of [AuS(CH$_2$)$_{15}$CO$_2$]$^-$ and [Au$_2$S(CH$_2$)$_{15}$CO$_2$H]$^-$ peaks (Figure 2-8) is also in agreement with this observation.

The spectra of the CO$_2$H film after 1.2 nm K deposition and water rinse are very similar to those of the original film. After water rinse, only very weak $^{39}$K$^+$ peak is found, indicating that most of K atoms are removed during water rinse. All these results suggest that high dose of K atoms do not damage the film backbone (CH$_2$)$_n$ and most of K atoms stay at the vacuum interface.

Figure 2-9 shows the IR spectra of a freshly-prepared CO$_2$H film (a), this film after ~2.0 nm K deposition (b), and this sample after K deposition and water rinse (c). The stretch of hydrogen-bonded C=O bond (1718 cm$^{-1}$) and non-hydrogen-bonded C=O bond (1742 cm$^{-1}$) disappear after K deposition. At the same time, two wide peaks appear at low frequency area and they are assigned as CO$_2^-$ symmetric stretch (1412, 1422 cm$^{-1}$) and CO$_2^-$ asymmetric stretch (1585 cm$^{-1}$ wide). The above data strongly suggest that all CO$_2$H groups react with the K atoms to form CO$_2$K$^+$ moieties on the vacuum interface. The CH$_2$ stretch peaks move to high frequency, and become a little broader (see Table 2), indicating the (CH$_2$)$_n$ chain becomes disordered after K deposition. After a water rinse,
Figure 2-7. [S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}K]\textsuperscript{-} and [S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}H]\textsuperscript{-} peaks from the negative ion spectra of the CO\textsubscript{2}H film with increasing amounts of K dose.
Figure 2-8. The intensity trend of [AuS(CH$_2$)$_{15}$CO$_2$H]$^-$ and [Au$_2$S(CH$_2$)$_{15}$CO$_2$]$^-$ peaks from negative ion spectra of the CO$_2$H film with K deposition.
Figure 2-9. IRS spectra of a CO$_2$H sample (a), this sample after 2.0 nm K deposition (b), and this sample after 2.0 nm K deposition and water rinse (c). Peak assignment can be referred in the caption of Figure 2-6. The CO$_2^-$ sym str (1412 and 1422) and asym str (1585 broad) peaks are narrower than those of CO$_2$CH$_3$/K system, indicating that the CO$_2^-$ structure is more symmetric in CO$_2$H/K system.
the CO$_2^-$ peaks disappear, and the spectrum is very similar to the spectrum from a CO$_2$CH$_3$ sample after K deposition and water rinse, indicating that the CO$_2$K moieties become CO$_2$H groups and a more ordered CO$_2$H film forms.

### 2.3.4 K on OH film

For the OH film, after 0.05 nm K dose, the $^{39}$K$^+$ peak dominates the positive ion spectrum, and all original positive ion peaks sharply decrease, very similar to the CO$_2$CH$_3$ and CO$_2$H systems. K$_2$O$^+$, K$_2$OH$^+$, (CH$_2$)$_n$OK$^+$ are found after the K deposition, suggesting K atoms react with OH groups to form OK moieties. Additionally, the appearance of the [S(CH$_2$)$_{16}$OK]$^-$ (m/z = 311.18 amu) peak (Figure 2-10a) is also in agreement with the formation of OK moieties. High resolution spectra of [S(CH$_2$)$_{16}$OH]$^-$ (m/z = 273.23 amu) are also shown in Figure 2-10b. It is found that after 1.03 nm K deposition, the [S(CH$_2$)$_{16}$OH]$^-$ peak still has considerable intensity, indicating the reaction between OH groups and K atoms is not complete.

The 1.20 nm K deposition and water rinse experiment was also applied to the OH film. The spectra before and after 1.2 K deposition and water rinse are very similar, and a very weak K$^+$ peak was found after water rinse. All these results suggest that a high dose of K atoms do not react with (CH$_2$)$_n$ and most of the K atoms stay at the vacuum interface.
Figure 2-10. [S(CH₂)₁₆OK]⁻ and [S(CH₂)₁₆OH]⁻ peaks from the negative ion spectra of the OH film with increasing amounts of K dose.
2.3.5 K on OCH₃ film

For the OCH₃ film, the $^{39}\text{K}^+$ peak dominates the positive ion spectra after K deposition. All original peaks continuously decrease, but not as fast as those in the CO₂H, CO₂CH₃ or OH systems (Figure 2-11). Although K₂O⁺ and K₂OH⁺ peaks are also found after K deposition, they are weak. In the negative spectra, the [S(CH₂)₁₆OK]⁻ peak is too weak to be clearly observed. At the same time, the [S(CH₂)₁₆OCH₃]⁻ peak continuously increases with K deposition (Figure 2-12a). Additionally, the [K+HS(CH₂)₁₆OCH₃]⁻ (m/z = 326.21 amu) peak increases with K dose (Figure 2-12b). From the above data, we believe that the interactions between K atoms and OCH₃ groups are relatively weak.

We compare the SIMS spectra of an OCH₃ film sample and this sample after 1.2 nm K deposition and a water rinse (Figure 2-13). They are very similar. The OCH₃-related peaks only slightly decrease, and OH film molecule related peaks are too weak to be found. The above data strongly suggest that a chemical reaction between K atoms and OCH₃ groups hardly occurs. The K atoms staying in the OCH₃ system may only form some complexes with the OCH₃ groups. Additionally, a very weak K⁺ peak remains after water rinse, indicating that most of K atoms stay at the vacuum interface. Obviously, the above results also suggest that K atoms do not react with the (CH₂)ₙ backbone.
Figure 2-11. Relative Au\(^+\) peak intensities of the CO\(_2\)H (diamond), CO\(_2\)CH\(_3\) (down triangle), OH (up triangle), OCH\(_3\) (circle) and CH\(_3\) (square) films with increasing amounts of K dose. I\(_0\) is the original peak intensity before K deposition, and I is the peak intensity after exposure of a certain amount of K vapor.
Figure 2-12. [S(CH₂)₁₆OCH₃]⁻ and [K+HS(CH₂)₁₆OCH₃]⁻ peaks from negative ion spectra of the OCH₃ film with increasing amounts of K dose.
Figure 2-13. $[\text{Au}_2\text{S(CH}_2\text{)}_{16}\text{X}]^-$ (X = OCH$_3$, OH) area of the negative ion spectra of an OCH$_3$ film (a), this sample after 1.2 nm K deposition and water rinse (b), and an OH film (c).
2.3.6 K on CH₃ film

Different from the previous four films, the K⁺ peak is very weak after 0.05 nm K deposition (Figure 2-14 left) for the CH₃ film. Positive ion signals of the CH₃ film slowly decrease with increasing K dose. It is also found that at first, K⁺ signal increases very slowly, but with more K on the surface, it increases more rapidly (Figure 2-14 right). The above results indicate that the initial sticking probability of K atoms on the CH₃ surface may be quite low. This observation is in qualitative agreement with the previously published result related to Na atom behavior on S(CH₂)₂CH₃ alkanethiol film³⁹. At the same time, the negative ion peaks increase with K deposition, suggesting that the surface work function decreases with K accumulation. Additionally, K⁺, KC⁺, KCₙHᵐ⁺, KₙOᵐ⁺, KₙSᵐ⁺ ion peaks are not clearly observed, suggesting that no chemical reactions occur.

SIMS spectra of the CH₃ film before and after 1.2 nm K deposition and water rinse are almost identical, indicating the film molecules are not damaged during K deposition. Additionally, the K⁺ peak becomes only one fifth of its intensity after water rinse, implying that most of the residual K atoms are washed away. We believe that the interactions between K atoms and CH₃ groups are very weak, and K atoms can freely move on the surface. Therefore, the large amount of K atoms remaining in the system most probably stay at the defect area, forming clusters, and only a small amount of them insert between film molecules or get to the Au/S interface.
Figure 2-14. Left, the positive ion spectra of a CH$_3$ film before (solid line) and after 0.05 nm K deposition (dash line). Right, the intensity trend of Au$^+$ and K$^+$ peaks from the positive ion spectra of a CH$_3$ film with increasing amounts of K dose.
2.3.7 Reactivity of different organic functional groups

SIMS data show that different organic functional groups have different reactivity with gaseous K atoms, which can be ranked as the following order: $\text{CO}_2\text{H} > \text{CO}_2\text{CH}_3 > \text{OH} > \text{OCH}_3 > \text{CH}_3$. The $\text{CO}_2\text{H}$, $\text{CO}_2\text{CH}_3$, and $\text{OH}$ groups react with K atoms, and form $\text{CO}_2\text{K}$ or $\text{OK}$ moieties, respectively. The $\text{OCH}_3$ groups and K atoms only form complexes at the vacuum interface, and very weak interaction between the $\text{CH}_3$ groups and K atoms is observed. The above results are consistent with experiences from traditional organic chemistry.

2.3.8 Sticking Coefficient of K atoms on Different Surfaces

To determine the sticking-coefficient of K atoms on different surfaces, QCM experiments are applied. Figure 2-15 shows the results. It is found that most of K atoms reaching the $\text{CO}_2\text{H}$, $\text{CO}_2\text{CH}_3$ and $\text{OH}$ surfaces stay at the vacuum interface. However, only about 40-60% of K atoms stay on the $\text{OCH}_3$ surface, and most of K atoms reaching the $\text{CH}_3$ surface rebound back to the vacuum. This result indicates that there is some relationship between the sticking coefficient and the interactions of metal/surface organic functional groups. Strong interactions correspond to a high sticking coefficient and weak interactions correspond to a low sticking coefficient.
Figure 2-15. The sticking coefficient of K atoms on CO$_2$H (up triangle), CO$_2$CH$_3$ (crossing), OH (down triangle), OCH$_3$ (diamond) and CH$_3$ (circle) surfaces. K dose is the thickness value from the reference surface (CO$_2$CH$_3$), i.e., I$_{ref}$, and I is the thickness value from the objective surface. QCM experiment on the CH$_3$ surface was repeated for three times; the experiment on any other surfaces was applied for only one time.
2.3.9 K vs Ti, Cr, Ca

K atoms are do not damage the -(CH$_2$)$_n$-CO$_2$- and -(CH$_2$)$_n$-O$^-$ moieties, and do not react with molecular backbone (-(CH$_2$)$_n$- chain). This is quite different from the behavior of some other active metal such as Ca, Ti or Cr, which have been found to “eat” a number of organic thin films during thermal deposition$^{17,18,20,40,41}$. One plausible explanation is the difference of radii and charge numbers of these metal ions. Positive ions of Ca, Ti or Cr with small radii and high charge numbers, are apt to form strong interactions with oxygen atoms or carbon atoms so that they destroy the C-O, C-C and C-H bonds. However, K$^+$ has a large radius and a low charge number, so K atoms or K$^+$ ions are friendly with organic thin films.

2.3.10 Low penetration of K atoms through the films

Previous documents show that if the main interactions between alkanethiol molecules are weak van der Waals forces, thermal movement of the film molecules leads to temporary vacancies, through which metal atoms can penetrate to the substrate$^{16,42,43}$. In this work, we find that most of the K atoms stay at the CO$_2$CH$_3$, CO$_2$H and OH surface with very weak penetration through the films even at high K dose. One reasonable explanation is that the first layer of K atoms react with surface organic functional groups to form K$^+$ ions and organic negative ions at the vacuum interface. The positive ions and
negative ions form a network at the interface. This network prohibits the film molecules from free movement. Thus metal atoms cannot penetrate through the ionic interface.

Since low dose of K (< 1.0 nm) can react with all surface CO$_2$H or CO$_2$CH$_3$ groups to form a CO$_2$K surface, using vapor K to modify CO$_2$H or CO$_2$CH$_3$ surfaces to form a CO$_2$K surface may be a good approach to prevent metal atoms from penetrating through alkanethiol films on Au substrates.

2.4 Conclusion

ToF-SIMS and IR were applied to study the behavior of K atoms on CO$_2$H, CO$_2$CH$_3$, OH, OCH$_3$, and CH$_3$-terminated alkanethiol SAMs on Au. Different organic functional groups show different reactivity. The reactivity of the five groups can be ranked as the following order: CO$_2$H > CO$_2$CH$_3$ > OH > OCH$_3$ > CH$_3$. Chemical reactions were found on the CO$_2$CH$_3$, CO$_2$H and OH surfaces, with CO$_2$K or OK moieties forming, respectively. A complex may form between OCH$_3$ groups and K atoms, and a very weak K/CH$_3$ interaction was observed. These observations are consistent with traditional organic chemistry. Furthermore, in the CO$_2$CH$_3$, CO$_2$H, OH and OCH$_3$ systems, most of K atoms stay at the vacuum interface with very weak penetration through the films. In all systems, K atoms do not react with the film molecule backbone (-CH$_2$)$_n$). Our results show that K may be applied to modify surface organic functional groups of alkanethiol SAMs. In addition, we believe that the ionic surface, such as CO$_2$K layer, may be a promising buffer layer to prevent metal atoms from penetrating through alkanethiol SAMs.
2.5 References


Chapter 3  

Controlling Au Penetration through Alkanethiol Self-Assembled Monolayers by Adjusting Intermolecular Interactions

3.1 Introduction

Vapor depositing Au on alkanethiol self-assembled monolayers (SAM) is a common way to prepare a Au/SAM/Au substrate sandwich structures\textsuperscript{1-6}. However, Au was found to penetrate through the SAMs very easily at room temperature\textsuperscript{7-11}. It has been found that if the interaction between metal atoms and surface organic functional groups is weak, the metal atom penetrates through the film. Theoretical calculations show that if the interactions between film molecules consist primarily of van der Waals forces, at room temperature, thermal energy can cause a small movement of the film molecules on the Au substrate\textsuperscript{12,13}. This movement results in temporary vacancies and the sizes of such vacancies are large enough for the leaking of metal atoms from the vacuum interface to Au/S interface\textsuperscript{14}.

One possible means to block metal penetration is to enhance the interactions between vapor deposited Au atoms and surface organic functional groups. For example, Au was found to form clusters at the vacuum interface when deposited on SH-terminated SAMs\textsuperscript{9,15,16}. Decreasing the substrate temperature is an alternative way to reduce the mobility of the SAM molecules. For example, Meed and coworkers cooled the SAM samples to liquid N\textsubscript{2} temperature to avoid Au atoms punching through the films \textsuperscript{1-6}. In
this paper, we examine the possibility of reducing Au penetration in another way by introducing strong interactions between film molecules.

In this work, Au deposition onto S(CH\(_2\)\(_{15}\))CH\(_3\), S(CH\(_2\)\(_{15}\))CO\(_2\)CH\(_3\), S(CH\(_2\)\(_{15}\))CO\(_2\)H, K-modified S(CH\(_2\)\(_{15}\))CO\(_2\)CH\(_3\) and K-modified S(CH\(_2\)\(_{15}\))CO\(_2\)H films are examined, and the effect of van der Waals forces, H-bonding, and ionic interactions on penetration of Au atoms is investigated. For CH\(_3\) and CO\(_2\)CH\(_3\)-terminated films, the interactions between molecules are mainly van der Waals interactions. For CO\(_2\)H-terminated films, the H-bonding between CO\(_2\)H groups has been reported\(^{17,18}\), and the energy of the H-bond is known to be higher than thermal energy at room temperature. Our previous work shows that CO\(_2\)K moieties form after K is deposited on the CO\(_2\)CH\(_3\) or CO\(_2\)H film, and the -(CH\(_2\))\(_n\)-chain of molecules is not destroyed by K atoms\(^{19,20}\). Thus, the interaction between the molecules of K modified CO\(_2\)CH\(_3\) or CO\(_2\)H films are mainly ionic interactions. These interactions are much larger than thermal energy, so we believe that metal penetration should be blocked.

A number of surface characterization techniques have been applied to investigate metal reactivity with SAMs, such as time-of-flight secondary ion mass spectrometry (ToF-SIMS)\(^{14,20-28}\), X-ray photoelectron spectroscopy (XPS)\(^{14,17,24,27-37}\), ion scattering spectroscopy (ISS)\(^{29,36,38,39}\), infrared reflection spectroscopy (IRS)\(^{14,15,17,23,24,27,40}\), scanning tunneling microscopy (STM)\(^{7-9,16,41}\), and near edge X-ray absorption fine structure spectroscopy (NEXAFS)\(^{42}\). Here, we focus on ToF-SIMS due to its high sensitivity and specificity to the chemistry of the films.

In previous work, we have utilized ToF-SIMS to examine the behavior of Al, Ag, Cu, K, Ti and other metals on a number of alkanethiol SAMs\(^{14,20-28}\). The special
advantage of these types of studies is that the molecular specificity associated with the mass spectra can be utilized to acquire detailed structural information by comparing with other techniques. For example, it has been found that AlOCH$_3^+$ ions are an indicator of Al atoms that deposit on the surface of the SAM on the OCH$_3$-terminated film, but that AlSH$_2^+$ ions are the indicator for Al penetrating through the organic thin film to the Au/S interface. Other types of cluster ions are also indicative of specific types of reaction chemistry. TiC$^+$ ions were found after Ti was deposited on an OCH$_3$ SAM, indicating that Ti atoms destroy the organic functional groups. When K was deposited on S(CH$_2$)$_{15}$CO$_2$CH$_3$ and S(CH$_2$)$_{15}$CO$_2$H films, the disappearance of molecular peaks and the increase of the S(CH$_2$)$_{15}$CO$_2$K$^-$ peak indicate that CO$_2$CH$_3$ and CO$_2$H groups react with K atoms to form CO$_2$K groups$^{19,20}$. Additionally, when K was evaporated on CH$_3$, CO$_2$CH$_3$ and CO$_2$H-terminated films, the K$^+$ signal on the CH$_3$ film was much weaker than those on the other two films, suggesting that K atoms form clusters rather than smooth layers on the CH$_3$ film$^{19,20}$. Hence there are a range of characteristic molecular peaks that provide simple and direct information about chemistry.

In this paper, a series of experiments are performed with ToF-SIMS where Au is evaporated on S(CH$_2$)$_{15}$CH$_3$, S(CH$_2$)$_{15}$CO$_2$CH$_3$, S(CH$_2$)$_{15}$CO$_2$H, K-modified S(CH$_2$)$_{15}$CO$_2$CH$_3$ and K-modified S(CH$_2$)$_{15}$CO$_2$H SAMs, respectively. No new mass peaks were found in any of the above mentioned systems, suggesting that no chemical reactions occur. After carefully analyzing the intensities of characteristic peaks, we find that Au atoms continuously penetrate through the S(CH$_2$)$_{15}$CH$_3$ and S(CH$_2$)$_{15}$CO$_2$CH$_3$ films, forming smooth underlayers below the organic thin films. Additionally, Au atoms partially penetrate through the S(CH$_2$)$_{15}$CO$_2$H film, and form filaments and mushroom-
like structures. However, Au atoms cannot penetrate through K-modified S(CH$_2$)$_{15}$CO$_2$CH$_3$ and S(CH$_2$)$_{15}$CO$_2$H films, and form islands at the vacuum interface. Our results demonstrate that enhancing the interactions between molecules is an effective way to reduce Au penetration. At the same time, we find ToF-SIMS is a convenient technique to distinguish different types of metal penetration.

3.2 Experiment

3.2.1 SAM Preparation

The procedure for preparing the S(CH$_2$)$_{15}$CO$_2$CH$_3$, S(CH$_2$)$_{15}$CO$_2$H, and S(CH$_2$)$_{15}$CH$_3$ SAMs has been described in detail previously$^{14,28}$. Briefly, ~200 nm Au was thermally deposited onto Si(001) wafers via a ~10 nm Cr adhesion layer. The Au substrates were immersed into 1.0 mM ethanol solutions of the alkanethiol molecules for ~2 days at room temperature. The samples were then removed from the solutions and thoroughly rinsed with ethanol, and were sonicated for 20 seconds to remove any possible physically adsorbed molecules. Finally, the samples were dried by blowing with pure nitrogen gas. The films were characterized with single wavelength ellipsometry, and contact angle measurements to ensure that the surfaces were clean and the packing was dense. The samples were put into the vacuum chamber and were characterized by ToF-SIMS prior to metal deposition. For convenience, the above films are referred to as CO$_2$CH$_3$, CO$_2$H, and CH$_3$ films, respectively.
3.2.2 Time-of-Flight Secondary Ion Mass Spectrometer

The ToF-SIMS instrument has been described previously\textsuperscript{43}. Briefly, the instrument consists of a loadlock, a metal deposition chamber, a preparation chamber, and a primary analysis chamber, each separated by a gate valve. Gallium ions of 15 keV were used as primary ions. The ions were focused into a 100 nm diameter beam that was rastered over a $300 \times 300 \ \mu\text{m}^2$ area during data acquisition. All spectra were acquired using a total ion dose of less than $10^{11}$ ions/cm$^2$. The relative standard deviation of peak intensities is within ±15% from both sample-to-sample and scan-to-scan. In all measurements, the base pressure in the analysis chamber is about $5.0 \times 10^{-10}$ torr.

3.2.3 Metal Deposition Chamber

Two metal sources were located side-by-side about 50 cm vertically above the SAM samples. The distance between the two sources is about 5 cm and they are separated by a 1mm thick stainless steel shutter. One source consists of a W basket filled with a Au slug (Aldrich, 99.99%). The other source is a K dispenser (SAES getters). Metal thickness was monitored by a quartz crystal microbalance (Maxtek TM400 controller, 6MHz crystal with a rough Au surface), placed about 47 cm from the sources.

3.2.4 Experiment Procedure

In our study, three film samples (CO$_2$CH$_3$, CO$_2$H, and CH$_3$, each about 6mm×6mm) were immobilized on a sample block and were put into vacuum. The SIMS spectra of
freshly prepared monolayers were taken as a control, and then the samples were transferred under vacuum to the metal deposition chamber, where Au atoms were deposited. After Au deposition, the samples were transferred back to the analysis chamber to acquire SIMS spectra. Each transfer time was about 4-6 min. The pressure of the deposition chamber before Au deposition was about $1.1 \times 10^{-9}$ Torr, and was $<1.0 \times 10^{-7}$ Torr during Au deposition. The Au deposition rate was controlled to about 0.01 nm/s. After SIMS analysis, the samples were redosed with additional Au. This process was repeated several times until the total Au thickness reached about 4.0 nm. One monolayer of Au is about 0.25 nm in thickness. One effective monolayer (one Au atom per organic functional group) corresponds to a thickness of 0.07 nm Au for all films.

When studying Au behavior on K-modified CO$_2$CH$_3$ and CO$_2$H SAMs, ~0.4 nm K was deposited on the CO$_2$CH$_3$ and CO$_2$H samples with a rate of ~0.002 nm/s. The samples were subsequently transferred to the analysis chamber. After SIMS measurements, the samples were transferred back to the metal deposition chamber for Au deposition. Au deposition and subsequent SIMS measurements were performed in the same fashion as described previously. Earlier data show that 0.4 nm of K can transforms almost all CO$_2$H groups into CO$_2$K groups, and 50-60% of CO$_2$CH$_3$ groups into CO$_2$K groups.$^{19,20}$

3.2.5 Sticking Coefficient Determination

Two QCM heads (both with 6MHz crystals, and ~200 nm Au attached on the crystals via a ~10 nm Cr adhesion layer) were immobilized side-by-side 50 cm under the Au source. A hand-controlled shutter was positioned ~2cm over the QCM heads. The first
crystal acts as the reference. This crystal has a rough surface and is normally used in our experiment. The second crystal has a smooth surface and is modified by the alkanethiol SAMs. The smooth QCM crystals (Cold Springs R&D, Syracuse, NY) were highly polished on top side to an rms roughness (tapping mode AFM) of 0.1-0.2 nm which resulted in the QCM SAM surfaces having near identical rms roughnesses to those of the SAMs prepared on silicon substrates. In our experiments, both crystals were simultaneously exposed to vapors. Au deposition rates were controlled in the same fashion as those reported earlier for the SIMS experiments.

3.3 Results and Discussion

ToF-SIMS spectra of freshly-prepared CH$_3$, CO$_2$CH$_3$ and CO$_2$H films on Au substrates have been described elsewhere$^{14,27,28,44-48}$. Briefly, characteristic peaks include $C_nH_m^\pm$, $S^-$, $SH^-$, $SC_nH_m^\pm$, $Au_n^\pm$, $Au_nS_mH_i^\pm$, $AuC_nH_m^\pm$, $AuSC_nH_m^\pm$, $AuM^\pm$, $Au_2M^-$, and $AuM_2^-$ ($M=S(CH_2)_15X$; $X=CH_3$, CO$_2$CH$_3$ and CO$_2$H). K-modified CO$_2$CH$_3$ and CO$_2$H films have been studied by ToF-SIMS previously$^{19,20}$ and the characteristic peaks are $K^+$, $K_2^+$, $K_2O^+$, $(CH_2)_nCO_2K_2^+$, $Au_nK_m^\pm$, $AuC_nH_m^\pm$, $AuS(CH_2)_15CO_2K^+$, and $(CH_2)_nCO_2^-$.

3.3.1 Au on CH$_3$ SAM

A partial spectrum of the CH$_3$ film following varying amounts of Au deposition is shown in Figure 3-1. The shape and intensity of the $AuS(CH_2)_{16}^+$ peak remains constant
Figure 3-1. AuS(CH$_2$)$_{16}^+$ ToF-SIMS spectra obtained from a CH$_3$ film with increasing amounts of Au deposition.
with Au deposition. Furthermore, the entire positive ion spectrum (in our experiment m/z = 0-1000) changes only slightly even after 4 nm Au deposition. This observation can be seen in the positive ion spectra between m/z = 0-200 as shown in Figure 3-2. The situation in the negative ion spectra is very similar to the positive ion spectra, i.e., the spectra only slightly change during Au deposition. A representative peak, \( \text{Au}_2\text{S(CH}_2\text{)}_{15}\text{CH}_3^- \), is shown in Figure 3-3. The thickness of a layer of close-packed Au atoms is about 0.25 nm, and 4 nm of Au corresponds to 16 layers. Since ToF-SIMS is a surface–specific technique and its information depth is generally one or two layers, it is unlikely that the Au atoms form smooth layers on top of the film, since they would greatly reduce the intensity of the signals from the underlying film. The results clearly suggest that most Au atoms penetrate through the CH\(_3\) film, and the film appears to “float” on these deposited atoms. Additionally, no new ion peaks are found during Au deposition, either positive or negative, indicating that no chemical reactions occur during Au evaporation.

Another possible explanation for our SIMS data is that Au atoms form very large clusters on top of the film, and because the surface area occupied by such clusters is small, the SIMS spectra only change slightly. However, several published papers\(^{7-9,36}\) show that in similar experiments, the evaporated Au atoms mainly form smooth layers under alkanethiol films. Therefore, we believe this is an unlikely scenario.

An interesting observation is that the \( \text{SO}_3^- \) and HSO\(_4^- \) peaks decrease significantly with Au deposition (Figure 3-4). They are weak peaks and are commonly found if the CH\(_3\) sample is prepared in an ambient environment. The appearance of these peaks
Figure 3-2. Positive ion ToF-SIMS spectra of a C_{15}CH_{3} film with Au thickness for 0, 1.03 and 3.93 nm.
Figure 3-3. $\text{Au}_2\text{S(C}_2\text{H}_5\text{)}_{15}\text{CH}_3^-$ ToF-SIMS spectra obtained from a CH$_3$ film with increasing amounts of Au deposition.
Figure 3-4. HSO$_4^-$ ToF-SIMS spectra obtained from a CH$_3$ film with increasing amounts of Au deposition
indicates that a small number of \(-\text{SH} \) groups are oxidized\textsuperscript{44,46}. As a comparison, most negative ion peaks change only slightly during this process. This observation can only be explained by accumulation of Au atoms on top of oxidized areas instead of by penetration. This result may be an explanation for previous STM results\textsuperscript{7}, in which most Au atoms, but not all, penetrate through alkanethiol films, even if the C-chains are relatively short.

3.3.2 Au on CO\textsubscript{2}CH\textsubscript{3} SAM

Gold deposition onto a CO\textsubscript{2}CH\textsubscript{3} film yields results that are similar to those for the CH\textsubscript{3} film. Both positive and negative ion spectra undergo slight changes during Au deposition. Two characteristic peaks, H\text{Au(S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}CH\textsubscript{3})\textsuperscript{+}} and \text{Au\textsubscript{2}S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}CH\textsubscript{3}\textsuperscript{-}} are shown in Figure 3-5. Additionally, no new peaks are observed. Obviously, Au behavior on the CO\textsubscript{2}CH\textsubscript{3} film behaves in a similar fashion to that of the CH\textsubscript{3} film, that is, Au atoms penetrate through the CO\textsubscript{2}CH\textsubscript{3} film and form smooth buried layers under the film. At the same time, no chemical reactions occur.

3.3.3 Au on CO\textsubscript{2}H SAM

For the CO\textsubscript{2}H film, characteristic positive ion peaks and negative ion peaks considerably decrease in intensity with Au deposition when compared with the CH\textsubscript{3} and CO\textsubscript{2}CH\textsubscript{3} systems. The trend for \text{Au\textsuperscript{+}} and \text{Au\textsuperscript{-}} intensity for the CH\textsubscript{3}, CO\textsubscript{2}CH\textsubscript{3} and CO\textsubscript{2}H
Figure 3-5. ToF-SIMS spectra obtained from a CO₂CH₃ film with increasing amounts of Au deposition. (a) HAuS(CH₂)₁₅CO₂CH₃⁺, and (b) Au₂S(CH₂)₁₅CO₂CH₃⁻.
films with Au deposition is shown in Figure 3-6. The ratio of $\text{Au}^3/\text{Au}_2\text{S}^-$ considerably increases for the CO$_2$H film (Figure 3-7). Clearly, Au atoms do not form smooth layers under the film. Here, a reasonable explanation is that a significant amount of Au atoms stay on top. Presumably, H-bonds between CO$_2$H groups prevent the Au atoms from penetrating. It is likely that the Au atoms on top of the film form clusters or islands instead of smooth layers at the vacuum interface, because after deposition of 4 nm of Au, over 40% of the original intensity of those characteristic peaks still remains (see Figure 3-8). Additionally, no new ion peaks were found during Au deposition, indicating no chemical reactions between CO$_2$H groups and Au atoms.

Evaporated Ag atoms remain on top of the S(CH$_2$)$_{15}$CO$_2$H SAM and slowly penetrate through it$^{31}$. We believe that a fraction of the Au atoms penetrate through the CO$_2$H film, because Au is relatively inactive if compared with Ag, and the Au-CO$_2$H interaction should be weaker than the Ag-CO$_2$H interaction. However, it is very difficult to determine which one is the main channel, penetrating or forming clusters at the vacuum interface, if only based on our SIMS data.

### 3.3.4 Au on 0.4 nm K Modified CO$_2$CH$_3$

To test the influence of chemically modified SAMs on Au penetration, one monolayer of K (~0.4 nm thick) was deposited on a CO$_2$CH$_3$ sample before Au evaporation. Previous work$^{19,20}$ has shown that atomic K atoms can react with CO$_2$CH$_3$ groups and form CO$_2$K moieties. However, 0.4 nm of K only reacts with 50-60% of
Figure 3-6. Relative intensities of $\text{Au}^+$ and $\text{Au}^-$ peaks as a function of evaporated Au thickness. $I_0$ is the original intensity of $\text{Au}^+$ or $\text{Au}^-$ peaks before Au deposition. (a) $\text{Au}^+$ peak, (b) $\text{Au}^-$ peak.
Figure 3-7. The ratio of $\text{Au}_3^-/\text{Au}_3\text{S}^-$ as a function of evaporated Au thickness.
Figure 3-8. AuS(CH$_2$)$_{15}$ ToF-SIMS spectra obtained from a CO$_2$H film with increasing amounts of Au deposition.
CO$_2$CH$_3$ groups, and there are still 40-50% CO$_2$CH$_3$ groups remaining. In the SIMS spectra, the CO$_2$CH$_3$ group related ion peaks, such as OCH$_3^+$, CO$_2$CH$_3^+$, Au$_2$S(CH$_2$)$_{15}$CO$_2$CH$_3^-$, are still clearly observed. These peaks decrease very rapidly with Au deposition. The behavior of CO$_2$CH$_3^+$ with Au deposition is shown in Figure 3-9. The CO$_2$CH$_3^+$ peak intensity trend compared to the Au/CO$_2$CH$_3$ system is shown in Figure 3-10. It is very clear that the signal decrease rate for the K-modified sample is much faster. All CO$_2$CH$_3$-related peaks drop to a low intensity after ~4.0 nm of Au deposition, strongly suggesting that most of the Au atoms stay on top of the K-modified CO$_2$CH$_3$ film instead of penetrating to the Au/S interface.

### 3.3.5 Au on 0.4 nm K-Modified CO$_2$H

To test the behavior of a CO$_2$K surface, 0.4 nm of K was evaporated onto a CO$_2$H SAM. This dose is known to convert all of the CO$_2$H groups to CO$_2$K moieties$^{19,20}$. Au deposition onto this surface yields several intriguing intensity changes. As shown in Figure 3-11, the Au$^+$ signal itself has almost disappeared after 4 nm of Au deposition. This result suggests, somewhat counter intuitively, that the Au atoms are remaining on the surface of the organic film. Clean metallic Au exhibits a very weak Au$^+$ signal intensity due to resonance charge neutralization$^{49}$ and the normally intense Au$^+$ emission arising from the Au-S interaction is effectively blocked by the metallic Au overlayer.

Additional intensity changes associated with the large molecular fragment C$_{15}$H$_{31}$CO$_2$K$_2^+$ and (CH$_2$)$_{15}$CO$_2^-$ as a function of Au deposition are shown in Figure 3-12.
Figure 3-9. CO$_2$CH$_3^+$ ToF-SIMS spectra obtained from the 0.4 nm K-modified CO$_2$CH$_3$ film with increasing amounts of Au deposition.
Figure 3-10. Relative intensities of $\text{CO}_2\text{CH}_3^+$ peaks as a function of evaporated Au thickness. $I_0$ is the original intensity of $\text{CO}_2\text{CH}_3^+$ peak before Au deposition. The signal increase after 0.26 nm Au deposition for K-modified $\text{CO}_2\text{CH}_3$ film is most probably due to increasing of sputtering yield.
Figure 3-11. Au⁺ ToF-SIMS spectra obtained from the K-modified CO₂H film with increasing amounts of Au deposition. The signal increase after 0.26 and 0.50 nm Au deposition is most probably due to increasing of sputtering yield.
Figure 3-12. Intensities of C_{15}H_{31}CO_2K^+ and (CH_2)_{15}CO^- peaks of the 0.4 nm K-modified CO_2H film as a function of evaporated Au thickness.
These signals steadily increase as the Au deposition occurs. This observation is consistent with the formation of nanoclusters of Au atoms forming on top of the SAM layer. It is well known that metal vapor deposition or metal nanoparticle deposition onto polymer surfaces significantly enhances the SIMS signal\textsuperscript{50-52}.

The 0.4 nm K-modified CO\textsubscript{2}CH\textsubscript{3} SAM exhibits similar behavior to the CO\textsubscript{2}H SAM. The Au\textsuperscript{+} signal decreases and the C\textsubscript{15}H\textsubscript{31}CO\textsubscript{2}K\textsubscript{2}\textsuperscript{+} and (CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}\textsuperscript{-} ions increasing during Au deposition. Hence, we believe this system also effectively blocks Au penetration.

### 3.3.6 Sticking Coefficient

In our experiment, a quartz crystal microbalance (QCM) is applied to monitor the thickness of Au deposition. It is obviously important to establish that the deposition rate and condensation efficiency is equivalent for all systems. A plot of relative condensation coefficient vs Au thickness for a reference QCM crystal is shown in Figure 3-13. This result clearly shows that the condensation coefficient is the same for all systems with an uncertainty of about 10%.

### 3.3.7 Exposure in Air

It is known that the weak SO\textsubscript{3}\textsuperscript{-} and HSO\textsubscript{4}\textsuperscript{-} peaks are found in the negative spectra. The SAMs are generally stable in air, at least for two hours (Figure 3-14a), indicating that the films are impermeable to oxygen in air. However, after 1.0 nm Au deposition,
Figure 3-13. Condensation coefficients of Au atoms on CH$_3$, CO$_2$CH$_3$, CO$_2$H, and 0.4 nm K-modified CO$_2$CH$_3$ and CO$_2$H films as a function of Au thickness on the reference QCM crystal.
Figure 3-14. A comparison of SO$_3^-$ peaks in the negative ion spectra of CH$_3$, CO$_2$CH$_3$ and CO$_2$H films before and after 2-hour exposure in air. (a) Freshly prepared samples, and (b) samples after 1 nm Au deposition.
different films show different oxidation-resistance. From Figure 3-14b, we find that the CH$_3$ and CO$_2$CH$_3$ systems are still impermeable to oxygen, but that the CO$_2$H system is not. Our explanation is that for the CH$_3$ and CO$_2$CH$_3$ systems, Au atoms evenly penetrate through the film and form smooth underlayers. The compact structure of the organic thin films remains intact and the films are still impermeable to oxygen. For the CO$_2$H film, 3-d Au clusters form on the surface. Theoretically, the H-bond network reduces the possibility of penetration of Au atoms through the CO$_2$H film as compared to the CH$_3$ or CO$_2$CH$_3$ films. But at some special areas where the H-bond network is weak, such as defect areas or domain edges, Au atoms easily pass through to the substrate. And after penetration of Au atoms, the H-bond network becomes weaker due to the change of substrate topography, resulting in more Au penetration in these areas. The compact structure of the CO$_2$H film is destroyed by the 3-d Au clusters, and oxygen molecules diffuse to the Au/S interface to oxidize the S atoms.

**3.3.8 Deposition Model**

Our data demonstrate that the penetration of Au atoms through alkanethiol SAMs can be controlled by adjusting the interactions between film molecules. For the CH$_3$ and CO$_2$CH$_3$ systems, only van der Waals interactions exist between film molecules, and Au atoms penetrate through the films evenly to form smooth layers under the film as illustrated in Figure 3-15a. H-bonding exists between CO$_2$H molecules, so that Au atoms form 3-d clusters at some special areas, and some of them stay on top of the film as
Figure 3-15. Schematic illustration of Au behaviors on different SAMs. (a) Even penetration and formation of smooth buried layers under the organic thin film, i.e., Au on CH₃ and CO₂CH₃ films. (b) Cluster formation below and on top of the film, i.e., Au on CO₂H film. (c) Island formation on top of the film, i.e., Au on K-modified CO₂CH₃ and CO₂H films.
illustrated in Figure 3-15b. Ionic interaction between film molecules is the strongest interaction in our study, and Au atoms are found to stay on top of the CO$_2$K layer to form islands as illustrated in Figure 3-15c. From these results, it can be conclude that enhancing the interactions between film molecules is an effective way to block, or at least reduce, Au atom penetration through alkanethiol SAMs on Au substrates.

Previously, a penetration mechanism of evaporated metals on SAMs has been proposed$^{14}$. With this model, metal atoms pass through thermally created temporary vacancies between film molecules. Here, we show that the CO$_2$K functionality is effective in blocking metal penetration. The strength of these types of ionic interactions (generally several hundred kJ/mol) is much higher than thermal energy at room temperature (~2.5 kJ/mol). However, H-bonding interactions are not effective enough to block penetration. Average H-bond energy is about 10-20 kJ/mol, larger than thermal energy at room temperature. So theoretically H-bonds between film molecules would block metal penetration. Our results show that Au penetration through the CO$_2$H film is still considerable. This point can be attributed to the structure of the CO$_2$H film$^{17,18,53-55}$. The disadvantage of the relative position of O atoms and H atoms make the strength of such H-bonds relatively weak, and it has been estimated that 20% or more CO$_2$H groups are free of H-bonding$^{17,18}$. Additionally, at the defect areas and domain edge, H-bond cannot form an effective network. Therefore, Au atoms can still considerably penetrate through the CO$_2$H film.
3.4 Conclusions

Au behavior on CH$_3$, CO$_2$H, CO$_2$CH$_3$, and 0.4 nm K-modified CO$_2$H SAMs has been investigated by ToF-SIMS. No apparent chemical reactions are found in any of systems due to chemical inertia of Au. Au atoms penetrate through CH$_3$ and CO$_2$CH$_3$ films evenly and form smooth buried layers under the organic thin films. The compact structure of the films remains. 3-d Au clusters are found below and on top of the CO$_2$H film. Most of Au atoms stay on top of 0.4 nm K-modified CO$_2$CH$_3$ and CO$_2$H films, indicating CO$_2$K layer is an effective buffer layer to block metal penetration. Au atoms are believed to form islands on the CO$_2$K layer.

Our results show that it is possible to control Au penetration through the alkanethiol SAMs by adjusting the interactions between film molecules. We find that enhancing interactions between film molecules is an effective way to reduce Au leaking through alkanethiol films on Au substrate. Van der Waals forces are weak and the films are rather permeable to Au atoms, such as the CH$_3$ and CO$_2$CH$_3$ films. The H-bond web in CO$_2$H film is also not strong enough, although the leaking of Au atoms becomes weaker. Ionic interaction is found to be sturdy enough to block penetration of Au atoms. We believe our results are beneficial for the fabrication of metal/organic thin film/metal sandwich structures, which is widely used in measurements of electric properties of organic thin films.

The data show that ToF-SIMS is an excellent tool for detecting chemical reaction, penetration and aggregation of deposited-Au on different organic thin films. For example, intensities of Au$^+$ peaks can be used as the indicator of Au penetration. For the even and
smooth penetration systems such as CH$_3$ and CO$_2$CH$_3$ system, Au$^+$ peaks only slightly change even after 16 layers of Au. When Au clusters form on top of the film, Au$^+$ peaks decrease to very low intensities after the same dose of Au evaporation. K-modified CO$_2$H and CO$_2$CH$_3$ systems are corresponding to this situation. For a partially penetrating system such as CO$_2$H system, the Au$^+$ peak intensity decreases, but not as much as for the CO$_2$K system.

Although ToF-SIMS can provide a lot of structural information about vapor-deposited metals/SAM systems, it has some drawbacks. One of them is that SIMS spectra cannot supply quantitative results. For example, we know that Au clusters form on top of the CO$_2$K surface, but SIMS spectra cannot provide the size and distribution of those clusters. At the same time, we also don’t know if those clusters are separated from Au substrates or are mushroom-like clusters. To resolve this problem, atomic force microscopy (AFM) investigation for above systems has been applied. Many interesting results have been found (Tad Daniel, PhD thesis, Penn State University, 2005).
3.5 References


Chapter 4

Ti / Alkanethiol Self-Assembled Monolayer Interfaces

4.1 Introduction

Vapor-depositing Ti on organic thin films is a common approach to prepare metal substrate/organic thin film/top metal contact sandwich structures, which are used in the measurement of electronic properties of some molecular electronic devices. Molecular electronics developed quickly during the last decade, and its main objective is the use of functional organic molecules to substitute traditional semiconductor circuits, thus greatly reducing the volume and power consumption. The molecules of interest can self-assemble on metal substrates, or be immobilized on metal substrates via LB film technique, while the top contact metals may be vapor-deposited on the films. Ti is commonly used as a contact metal because it has good adhesive properties with organic surfaces. Because the structure of metal/organic interfaces will affect the measurement results, understanding the Ti/organic thin film interfaces is very important.

Ti can also be applied as an adhesion-promoting layer between metal coating and polymers, for example, enhancing the adhesion between Cu and polyimide in the manufacture of ultra-large-scale-integration and giga-scale-integration. At the same time, the Ti layer can also prevent metal atoms from defusing into polymers. Since Ti is such a useful contact metal on the surface of polymers, understanding the structure of the
Ti/polymer interfaces is necessary. During the last decade, great efforts were applied to this topic\textsuperscript{30-38}. It has been found that Ti is so active that it is able to easily react with most organic functional groups, and even very inert groups, such as CF\textsubscript{3}\textsuperscript{30,33}. This is the reason why Ti performs good adhesion behavior on most organic surfaces and prevents subsequent metal atoms from defusing into polymers. Unfortunately, Ti/polymer interfaces are complex because polymer surfaces are generally irregular and composed of several kinds of organic functional groups. Alkanethiol self-assembled monolayer (SAM) systems are simple model systems for the studies of Ti/polymer interfaces\textsuperscript{31,32,36-39}. Compared with the polymer surfaces, the main advantage of alkanethiol SAMs is that only one kind of organic functional group rests at the surface\textsuperscript{40-42}.

So far, studies of Ti behavior on several alkanethiol SAMs have been reported\textsuperscript{31,32,36-38}. Ti was found to damage organic functional groups, forming Ti\textsubscript{x}C\textsubscript{y} complexes. In recent years, Ti has been found to damage molecular wire SAMs on Au substrates\textsuperscript{36,39}. Although there are a number of papers that have been published on this topic, more detailed and quantitative information is still needed to illustrate Ti/SAM interfaces. At the same time, Ti/SAM interfaces have not been systemically studied by secondary ion mass spectrometry (SIMS), which is a very important surface analysis technique with a number of special advantages. Therefore, a systematic SIMS investigation would be able to greatly reinforce the understanding of Ti/SAM interfaces.

In previous work, we have utilized time-of-flight SIMS to examine the behavior of vapor-deposited Al, Au, Ag, Cu, K, and other metals on a number of alkanethiol films\textsuperscript{32,35,37-39,43-48}. ToF-SIMS has proven to be a very good technique to acquire
information about chemical reactions, metal penetration, cluster formation and damage of organic molecules.

Here, ToF-SIMS is applied to investigate the behavior of vapor-deposited Ti atoms on S(CH$_2$)$_{15}$CO$_2$H, S(CH$_2$)$_{15}$CO$_2$CH$_3$, S(CH$_2$)$_{15}$CH$_3$, and S(CH$_2$)$_{15}$CO$_2$K films. Different doses of Ti were vapor-deposited on the CO$_2$H, CO$_2$CH$_3$ and CH$_3$ SAMs and SIMS spectra were acquired. Careful analysis of these spectra supplies chemical and structural information about these Ti/SAM systems. Additionally, the sticking coefficient of Ti atoms on these films was also tested. A schematic model of Ti behavior on different surfaces was established based upon the combination of the above data. The CO$_2$K surface is interesting because it can prevent Au atoms from penetrating through the alkanethiol SAMs. In this work, we hope it can prevent organic molecules from being damaged by vapor Ti atoms.

### 4.2 Experiment

#### 4.2.1 SAM Preparation

The procedure for preparing the S(CH$_2$)$_{15}$CO$_2$H, S(CH$_2$)$_{15}$CO$_2$CH$_3$, and S(CH$_2$)$_{15}$CH$_3$ SAMs has been described in detail previously$^{44-46}$. Briefly, ~200 nm Au was thermally deposited onto Si(001) wafers via a ~10 nm Cr adhesion layer. The Au substrates were immersed into 1.0 mM ethanol solutions of the alkanethiol molecules for ~2 days at room temperature. The samples were taken out from the solutions and thoroughly rinsed by ethanol, and were sonicated for 20 seconds to remove any possible
physically adsorbed film molecules. Finally, the samples were dried by flowing pure nitrogen gas. The film samples were characterized with single wavelength ellipsometry, and contact angle measurements to ensure dense packing and clean surfaces. The S(CH$_2$)$_{15}$CO$_2$K film was prepared by evaporating 0.4 nm of K atoms on a S(CH$_2$)$_{15}$CO$_2$H film$^{48, 49}$.

### 4.2.2 Time-of-Flight Secondary Ion Mass Spectrometer

The ToF-SIMS instrument has been described previously$^{50}$. Briefly, the instrument consists of a loadlock, a metal deposition chamber, a preparation chamber, and a primary analysis chamber, each separated by a gate valve. Gallium ions of 15 keV were used as primary ions. The ions were focused into a 100 nm diameter beam that was rastered over a 300 × 300 µm$^2$ area during data acquisition. All spectra were acquired using a total ion dose of less than 10$^{11}$ ions/cm$^2$. The relative standard deviation of peak intensities is within ±10% from both sample-to-sample and scan-to-scan. In all measurements, the base pressure in the analysis chamber is about 5.0×10$^{-10}$ torr.

### 4.2.3 Metal Deposition Chamber

With the metal deposition chamber, two metal sources were located side-by-side about 50 cm vertically above the SAM samples. The distance between the two sources is about 5 cm and they are separated by a 1 mm thick stainless steel shutter. One source consists of a W basket filled with a Ti slug (Aldrich, 99.99%). The other source is a K
dispenser (SAES getters). Metal thickness was monitored by a quartz crystal microbalance (Maxtek TM400 controller, 6MHz crystal with rough Au surface), placed beside the samples.

### 4.2.4 Experiment Procedure

In our study, a batch of samples (CO$_2$CH$_3$, CO$_2$H, and CH$_3$, each about 6mm×6mm) were immobilized on a sample block and were put into vacuum. The SIMS spectra of freshly prepared monolayers were taken as a control, and then the samples were transferred under vacuum to the metal deposition chamber, where Ti atoms were deposited. After Ti deposition, the samples were transferred back to the analysis chamber to acquire SIMS spectra. Each transfer time was about 4-6 min. The samples are then taken out from the vacuum chamber, rinsed by 5% HF aqueous solution to remove any Ti overlayer, and analyzed by SIMS again. The above process was repeated for each group of samples. The only difference is an increase of Ti dose. In our study, 8-10 batches of samples were used until Ti thickness reached 2-5 nm, depending on the samples. The pressure of the deposition chamber before Ti deposition was about 1.1×10$^{-9}$ Torr, and was <1.0×10$^{-6}$ Torr during Ti deposition. The Ti deposition rate was controlled to about 0.002nm/s. One monolayer of Ti is about 0.25 nm in thickness. One equivalent monolayer (one Ti atom per organic functional group) corresponds to a thickness of 0.067 nm Ti for all films.

When studying damage of Ti atoms on K-modified CO$_2$H SAMs, ~0.4 nm K was deposited on the CO$_2$H samples with a rate of ~0.002 nm/s. Earlier data show that 0.4 nm
of K can transform almost all CO$_2$H groups into CO$_2$K groups$^{48,49}$. The samples were subsequently transferred to the analysis chamber. After SIMS measurements, the samples were transferred back to the metal deposition chamber for Ti deposition. About 1.50 nm Ti was deposited on the sample, and subsequent SIMS measurements and HF rinse were performed in the same fashion as described previously.

### 4.2.5 Sticking Coefficient Determination

To determine the sticking coefficient of Ti atoms on different organic surfaces, QCM experiments are applied. Two QCM heads (both with 6MHz crystals, and ~200 nm Au attached on the crystals via a ~10 nm Cr adhesion layer) were immobilized side-by-side 50 cm under the Ti source. A hand-controlled shutter was positioned ~2 cm over the QCM heads. The first crystal acts as the reference. This crystal has a rough surface and is normally used in our experiment. The second crystal has a smooth surface and is modified by the alkanethiol SAMs. The smooth QCM crystals (Cold Springs R&D, Syracuse, NY) were highly polished on the top side to an rms roughness (tapping mode AFM) of 0.1-0.2 nm which resulted in the QCM SAM surfaces having near identical rms roughnesses to those of the SAMs prepared on silicon substrates. In our experiments, both crystals were simultaneously exposed to vapors. Ti deposition rates were controlled in the same fashion as those reported earlier for the SIMS experiments.
4.3 Results & Discussion

ToF-SIMS spectra of the CH$_3$, CO$_2$CH$_3$ and CO$_2$H films on Au substrates have been described elsewhere$^{44-46,51-56}$. Briefly, characteristic peaks include C$_n$H$_m^\pm$, S$^-$, SH$^-$, SC$_n$H$_m^\pm$, Au$_n^\pm$, Au$_n$S$_m$H$_l^\pm$, AuC$_n$H$_m^\pm$, AuSC$_n$H$_m^\pm$, AuM$^\pm$, Au$_2$M$^-$, and AuM$_2^-$ (M=S(CH$_2$)$_{15}$X; X=CH$_3$, CO$_2$CH$_3$ and CO$_2$H). The SIMS characteristic peaks of the CO$_2$K film are K$^+$, K$_2^+$, K$_2$O$^+$, (CH$_2$)$_n$CO$_2$K$_2^+$, Au$_n$K$_m^\pm$, AuC$_n$H$_m^\pm$, AuS(CH$_2$)$_{15}$CO$_2$K$^-$, and (CH$_2$)$_n$CO$_2$.$^{48,49}$

4.3.1 CO$_2$H Film

Figure 4-1 and Figure 4-2 shows the positive and negative SIMS spectra of seven CO$_2$H film samples with different amounts of Ti deposition. We find that characteristic peaks of the CO$_2$H film (CO$_2$H$^+$, AuS(CH$_2$)$_{15}$, and Au$_2$S(CH$_2$)$_{15}$CO$_2$H) greatly decrease after 0.13 nm Ti deposition. This observation can be explained by two possible reasons: one is that Ti atoms react with CO$_2$H groups, to form CO$_2^-$ and Ti$^{n+}$ ions (here n is estimated from 1-2) at the vacuum interface; the other is the overlayer of Ti atoms hinder the escape of organic molecule fragments below it.

The appearance of a strong TiO$^+$ signal implies that Ti atoms react with CO$_2$H groups. Ti$^+$ and TiO$^+$ peaks increase with increasing Ti dose and reach a plateau after 0.60 nm of Ti, then decrease a little with more Ti. 0.60 nm of Ti is about equal to 2.4 layers of close-packed Ti atoms. Therefore, a possible explanation for decreasing of the
Figure 4-1. Positive ion spectra of the CO$_2$H samples with increasing amount of Ti deposition. a, Ti$^+$; b, CO$_2$H$^+$; c, $^{48}$TiO$^+$; d, $^{48}$TiC$^+$ and SC$_2$H$_4^+$. 
Figure 4-2. Negative ion spectra of the CO₂H samples with increasing amount of Ti deposition. a, AuS(CH₂)₁₅⁻; b, Au₂S(CH₂)₁₅CO₂H⁻.
Ti$^+$ and TiO$^+$ signal is that these ions mainly come from the Ti/CO$_2$H interface, and the overlayers of additional Ti on the Ti/CO$_2$H interface would hinder the Ti$^+$ and TiO$^+$ ions from escaping. Additionally, metallic Ti is an electron-donor. Accumulation of Ti atoms on the sample surface leads to a decrease of surface work function. This effect may also reduce the intensity of positive ions$^{51}$.

The TiC$^+$ peak arises after 0.13 nm of Ti deposition. The appearance of this peak indicates that Ti atoms damage organic functional groups$^7$, as well as the (CH$_2$)$_n$ chain, forming Ti$_x$C$_y$ complexes$^{32,37,39}$. From Figure 4-1d, we find that the TiC$^+$ peak decreases with increasing Ti dose. This situation can be explained by overlayers of Ti atoms and a decrease of surface work function.

Since ToF-SIMS has a very shallow information depth, a Ti overlayer on top of the organic thin film would greatly affect the intensities of the SIMS spectra. Thus, it is difficult to estimate the damage degree of CO$_2$$^-$ moieties. Therefore, a rinse of 5% HF aqueous solution was applied to remove the Ti overlayers on the samples. A control experiment was applied before the experiment. The result shows that no detectable destruction is found when a CO$_2$H film sample is rinsed by 5% HF.

Figure 4-3 shows that the Ti$^+$ peak from a CO$_2$H sample with 1.42 nm of Ti on it and this sample after HF rinse. Obviously most of the Ti was removed. This result suggests that most of the Ti atoms stay on the vacuum interface, with weak penetration through the organic thin film. This result is a sharp contrast to the behavior of vapor-

* Here, damage is also one kind of chemical reaction. However, we use “damage” because the reaction products are not stoichiometric compounds, but some amorphous materials.
Figure 4-3. $^{48}\text{Ti}^+$ peak of a CO$_2$H sample after 1.42 nm Ti deposition (a) and this sample after 1.42 nm Ti deposition and 5% HF rinse (b).
Figure 4-4. SIMS spectra of the CO$_2$H samples after Ti deposition and HF rinse. a, CO$_2$H$^+$; and b, Au$_2$S(CH$_2$)$_{15}$CO$_2$H$^-$. 
deposited Au atoms on the alkanethiol SAMs\textsuperscript{17}, in which large amounts of Au atoms penetrate through the CO\textsubscript{2}H film. Figure 4-4 shows two characteristic peaks, CO\textsubscript{2}H\textsuperscript{+} and Au\textsubscript{2}S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}H\textsuperscript{-}. Compared with the spectra with Ti atoms on the samples, the decrease of these two peaks is much slower. We find that even after 0.81 nm Ti deposition and HF rinse, these peaks are still visible. Only after 1.42 nm of Ti deposition and HF rinse, these peaks become very weak. This result suggests that at the initial steps, most CO\textsubscript{2}H groups react with Ti atoms, forming CO\textsubscript{2}\textsuperscript{-} and Ti\textsuperscript{n+} ions\textsuperscript{*}. With more Ti dose on the sample, the CO\textsubscript{2}\textsuperscript{-} moieties are gradually damaged, forming Ti\textsubscript{x}O\textsubscript{y} and Ti\textsubscript{x}C\textsubscript{y} complexes. Additionally, after 1.42 nm Ti deposition and HF rinse, not only do the initial peaks become weak, but also few new peaks appear. A reasonable explanation is amorphous carbon or graphite-like structures covering the surface after Ti deposition and HF rinse. The irregularity of the surface lead to no new characteristic peaks.

\textbf{4.3.2 CO\textsubscript{2}CH\textsubscript{3} Film}

Figure 4-5 shows CO\textsubscript{2}CH\textsubscript{3}\textsuperscript{+}, TiOCH\textsubscript{3}\textsuperscript{+}, TiO\textsuperscript{+}, TiC\textsuperscript{+}, OCH\textsubscript{3}\textsuperscript{-} and Au\textsubscript{2}S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}CH\textsubscript{3}\textsuperscript{-} peaks of seven CO\textsubscript{2}CH\textsubscript{3} samples with different amounts of Ti doses on them. Characteristic peaks of the CO\textsubscript{2}CH\textsubscript{3} film (CO\textsubscript{2}CH\textsubscript{3}\textsuperscript{+}, OCH\textsubscript{3}\textsuperscript{-}, and Au\textsubscript{2}S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}CH\textsubscript{3}) decrease with the increasing amounts of Ti deposition. The appearance of TiOCH\textsubscript{3}\textsuperscript{+}, TiO\textsuperscript{+}, TiC\textsuperscript{+} peaks indicates that the Ti atoms react with CO\textsubscript{2}CH\textsubscript{3}

\textsuperscript{* For some unknown reasons, CO\textsubscript{2}Ti\textsuperscript{+} signals are too weak to be clearly distinguished in the Ti/CO\textsubscript{2}H system.
Figure 4-5. Positive and negative ion spectra of the CO$_2$CH$_3$ samples with increasing amount of Ti deposition. a, CO$_2$CH$_3^+$; b, $^{48}$TiOCH$_3^+$ and C$_6$H$_7^+$; c, $^{48}$TiO$^+$; d, $^{48}$TiC$^+$ and SC$_2$H$_4^+$; e, OCH$_3^-$; f, Au$_2$S(CH$_2$)$_{15}$CO$_2$CH$_3$. 
Figure 4-5. Continued
groups and damage them, forming Ti$_{x}$O$_{y}$ and Ti$_{x}$C$_{y}$ complexes. The trend of TiO$^{+}$ and TiOCH$_{3}$$^{+}$ signals is very similar to the TiO$^{+}$ signal in Ti/CO$_{2}$H system, showing similarities of these two systems.

However, compared with the Ti/CO$_{2}$H system, at the same dose of Ti, the decrease of original characteristic peaks from the CO$_{2}$CH$_{3}$ system is slower. For example, after 0.13 nm Ti deposition, the CO$_{2}$H$^{+}$ peak from the CO$_{2}$H system becomes $\sim$15% of its original intensity, but the CO$_{2}$CH$_{3}$$^{+}$ peak from the CO$_{2}$CH$_{3}$ system still has 50% of its original intensity. The Au$_{2}$S(CH$_{2}$)$_{15}$CO$_{2}$CH$_{3}$$^{-}$ peak from the CO$_{2}$CH$_{3}$ system is clear even after 0.36 nm Ti deposition, but the Au$_{2}$S(CH$_{2}$)$_{15}$CO$_{2}$H$^{-}$ peak from the CO$_{2}$H system decreases to noise level only after 0.25 nm Ti deposition. All these data suggest that (1) the Ti/CO$_{2}$CH$_{3}$ interactions are weaker than Ti/CO$_{2}$H interactions, and (2) distribution of Ti atoms on the CO$_{2}$CH$_{3}$ surface is not as even as that on the CO$_{2}$H surface.

A rinse of 5% HF aqueous solution was also applied to remove Ti atoms on the CO$_{2}$CH$_{3}$ surface. Similar to the CO$_{2}$H system, almost all Ti atoms are removed successfully, indicating weak penetration of Ti atoms. Figure 4-6 shows CO$_{2}$CH$_{3}$$^{+}$ and AuS(CH$_{2}$)$_{15}$CO$_{2}$H$^{-}$ peaks from the CO$_{2}$CH$_{3}$ samples after Ti deposition and HF rinse. It is clear that the CO$_{2}$CH$_{3}$ groups gradually react with Ti atoms, and most CO$_{2}$CH$_{3}$ groups are consumed after 0.81 nm of Ti. This observation is in disagreement with previous conclusions from XPS results, in which 0.2 nm Ti is believed to be enough to react with all CO$_{2}$CH$_{3}$ groups$^{31}$. The AuS(CH$_{2}$)$_{15}$CO$_{2}$H$^{-}$ peak appears after 0.13 nm Ti deposition and HF rinse, indicating that some of the CO$_{2}$CH$_{3}$ groups react with atomic Ti to form CO$_{2}$$^{-}$ moieties, and CO$_{2}$$^{-}$ moieties become CO$_{2}$H groups when the sample is rinsed by the
Figure 4-6. SIMS spectra of the CO₂CH₃ samples after Ti deposition and HF rinse. a, CO₂CH₃⁺; and b, Au₂S(CH₂)₁₅CO₂H⁻.
The AuS(CH$_2$)$_{15}$CO$_2$H$^-$ signal gradually decreases if more Ti dose is added on the CO$_2$CH$_3$ samples. Obviously, high dose of Ti on the CO$_2$CH$_3$ sample subsequently damages the CO$_2^-$ moieties. Figure 4-6b shows that 1.42 nm (~21 equivalent monolayers) of Ti damages most CO$_2^-$ moieties.

### 4.3.3 CH$_3$ Film

Compared with the CO$_2$H and CO$_2$CH$_3$ system, Ti$^+$ signal from the CH$_3$ system is very weak (Figure 4-7a) at the beginning. Two possible reasons may contribute to this observation. One is low sticking coefficient of Ti atoms on the CH$_3$ surface; the other is formation of three-dimensional Ti clusters on the CH$_3$ surface. To distinguish between these reasons, a QCM experiment is applied. The result shows that the sticking coefficient of Ti on the CH$_3$ surface is pretty low at the beginning, about only 20% (Figure 4-7b). However, at the same Ti dose, Ti$^+$ signal from the CH$_3$ system is still much lower than 20% of Ti$^+$ signal from the CO$_2$H and CO$_2$CH$_3$ systems. Therefore, the second reason likely also occurs.

Figure 4-8 shows Ti$^+$, AuS(CH$_2$)$_{16}^+$, TiC$^+$ and HAuS(CH$_2$)$_{15}$CH$_3^-$ peaks from the CH$_3$ samples with different amount of Ti doses on them. Here, the values of Ti doses are the original data from the QCM monitor and not calibrated by sticking coefficient. Ti$^+$ signal increases before 3.70 nm Ti, but greatly decreases after 5.48 nm Ti on the sample. The decreasing of Ti$^+$ should be corresponding to that Ti atoms totally cover the CH$_3$ surface, because at this dose, almost all original characteristic peaks of the CH$_3$ film, such
Figure 4-7. Ti$^+$ peak intensity and sticking coefficient of Ti atoms on different surfaces as a function of Ti dose. (a) Normalized Ti$^+$ intensities from the CO$_2$H (square), CO$_2$CH$_3$ (circle) and CH$_3$ (triangle) samples. (b) Sticking coefficient of Ti atoms on the CO$_2$H (square), CO$_2$CH$_3$ (circle), CH$_3$ (triangle), and 0.4 nm K-modified CO$_2$H (diamond). Here, Ti dose ($I_{\text{ref}}$) is the thickness value from the reference QCM crystals (rough Au surface). The sticking coefficient is the ratio of the thickness value from the SAM-modified QCM crystals ($I$) to the thickness value from the reference QCM crystals ($I_{\text{ref}}$).
Figure 4-8. Positive and negative ion spectra of the CH₃ samples with increasing amount of Ti deposition. a, $^{48}$Ti⁺; b, AuS(CH₂)₁₆⁺; c, $^{48}$TiC⁺ and SC₂H₄⁺; d, HAuS(CH₂)₁₅CH₃⁻.
as AuS(CH$_2$)$_{16}^+$, TiC$^+$ and HAuS(CH$_2$)$_{15}$CH$_3^-$ disappear. The TiC$^+$ peak becomes apparent after 1.42 nm Ti deposition, suggesting that Ti atoms start to damage the CH$_3$ groups as well as (CH$_2$)$_n$ chains. The AuS(CH$_2$)$_{16}^+$ signal starts to decrease after 2.21 nm of Ti, indicating that Ti considerably damages the CH$_3$ film at this dose. HAuS(CH$_2$)$_{15}$CH$_3^-$ signal increases a little initially, and then decreases with more Ti on the sample. Here, the electron-donor effect of Ti atoms can explain the beginning increase$^{51}$, and the coverage and destruction effect of Ti finally diminishes the negative ion signal.

To evaluate the Ti destruction on CH$_3$ surface, Ti is also removed by 5% HF solution. We find that most of the Ti atoms are successfully removed by comparing the Ti$^+$ signal before and after HF rinse, indicating that the penetration of Ti atoms is weak. Figure 4-9 shows the AuS(CH$_2$)$_{16}^+$ and HAuS(CH$_2$)$_{15}$CH$_3^-$ peaks of the CH$_3$ samples after Ti deposition and HF rinse. These spectra are very similar to the spectra before HF rinse (see Figure 4-8). It is easy to find that 2.21 nm of Ti starts to considerably damage the CH$_3$ film, and 5.48 nm Ti is sufficient to completely destroy all S(CH$_2$)$_{15}$CH$_3$ molecules. Comparing the SIMS spectra before and after HF rinse, we can conclude that when Ti forms clusters on the CH$_3$ surface, most S(CH$_2$)$_{15}$CH$_3$ molecules under the Ti clusters are damaged. The damage follows an island-enlargement process.

The Ti/CH$_3$ interface has been studied by XPS and IR$^{31,36}$, but the data are not detailed. Recently, this interface was carefully characterized using several techniques via a collaboration between the Allara group and our group$^{38}$. However, multi-technique characterization of a special system is not the emphasis here. Interested readers are referred to reference 43.
4.3.4 CO$_2$K Film

Our previous work mentioned that a CO$_2$K layer at the vacuum interface can effectively prevent vapor-deposited Au atoms from diffusion into the Au/S interface at room temperature$^{17}$. In this work, we try to test if such an ionic surface is effective to prevent vapor deposited Ti atoms from damaging organic molecules. The CO$_2$K surface is prepared by depositing 0.4 nm of K onto a CO$_2$H sample (detailed procedure see Chapter 2 and 3). Then 1.50 nm of Ti is deposited on this sample. Figure 4-10 shows CO$_2$H$^+$ and AuS(CH$_2$)$_{15}^-$ peaks of three samples. The first one is a freshly prepared CO$_2$H film sample. The second one is a CO$_2$H sample after 0.4 nm K deposition and rinsed by 5% HF aqueous solution. The third one is a CO$_2$H sample after 0.4 nm K deposition and 1.50 nm Ti deposition and a rinse of 5% HF. Weak CO$_2$H$^+$ and AuS(CH$_2$)$_{15}^-$ peaks are observed after Ti deposition and HF rinse, indicating most CO$_2^-$ moieties are destroyed by 1.50 nm of Ti. This result suggests that the CO$_2$K layer is not an effective buffer layer to prevent organic molecules from Ti destruction.

4.3.5 Ti/SAM Interfaces

The sticking coefficient of Ti atoms on the CO$_2$K surface is found to be about 100% (see Figure 4-7b), indicating that nearly all Ti atoms reaching the CO$_2$K surface stay on it. This result suggests that Ti/CO$_2^-$ interactions are strong. Comparing the sticking coefficient if Ti atoms on the CO$_2$H, CO$_2$CH$_3$, CH$_3$ and CO$_2$K surfaces, we find that the O-contained surfaces have strong interactions with the Ti atoms. The reason may
Figure 4-9. SIMS spectra of the CH₃ samples after Ti deposition and HF rinse. a, \( \text{AuS(CH}_2\text{)}_{16}^+ \); and b, \( \text{HAuS(CH}_2\text{)}_{15}\text{CH}_3^- \).
Figure 4-10. CO$_2$H$^+$ and AuS(CH$_2$)$_{15}$$^-$ peaks from (a) a freshly prepared CO$_2$H film sample; (b) a CO$_2$H sample after 0.4 nm K deposition and rinsed by 5% HF aqueous solution, (c) a CO$_2$H sample after 0.4 nm K deposition and 1.50 nm Ti deposition and a rinse of 5% HF.
Figure 4-11. Schematic illustration of Ti behavior on different alkanethil SAMs. (a) Layer-by-layer top-down reaction-destruction mode (for example, Ti on the CO$_2$H film) vs island-enlargement reaction-destruction mode (for example, Ti on the CH$_3$ film). Thick arrows represent the incoming Ti atoms, and the thin arrows represent the rebounded Ti atoms. (b) Final result of Ti on alkanethiol SAMs.
be that the O-atom is a good electron acceptor and Ti is an electron donor. The CH$_3$ group is not a good electron acceptor, leading to a low sticking coefficient of Ti atoms.

Because of the shallow information depth of SIMS, the doses for disappearance of molecular ion peaks can be regarded as the critical values at which Ti atoms cover all the organic surfaces. The values for the CO$_2$H, CO$_2$CH$_3$ and CH$_3$ surfaces are 0.25, 0.60 and 5.48 nm (3.84 nm after calibration) of Ti, respectively. The difference of these values implies the different intensity of Ti/surface organic functional group interactions: Ti/CO$_2$H > Ti/CO$_2$CH$_3$ > Ti/CH$_3$. The different doses also imply information about Ti clusters. Since 0.25 nm is equal to the thickness of one close-packed layer of Ti atoms, Ti growth on the CO$_2$H surface is like a layer-by-layer mode. On the contrary, Ti forms isolated small islands on the CH$_3$ surface at the beginning, and the islands gradually grow to cover all of the CH$_3$ surface at high Ti doses. Obviously, there is some relationship between the metal growth modes and Ti atoms/organic functional groups interactions. Strong interactions lead to a layer-by-layer growth mode. Weak interactions lead to an island-enlargement growth process. A schematic illustration of the formation of Ti clusters on different surfaces is shown in Figure 4-11a.

Chemical reactions are observed between Ti atoms and surface organic functional groups. One interesting observation is that most surface organic functional groups under Ti overlayers are reacted. This observation is easy to understand because Ti is a very active metal. However, there is some difference among different systems. For example, initially, CO$_2$H and CO$_2$CH$_3$ groups react with Ti atoms to form CO$_2^-$Ti$^+$, and high doses of Ti gradually damages CO$_2^-$ moieties as well as (CH$_2$)$_n$. This damage process is like a top-down mode. At the same time, it is found that as long as the CH$_3$ groups and (CH$_2$)$_n$
are under the Ti clusters, they are damaged. This damage process is like an island-enlargement process. Additionally, we notice that even in the CO$_2$H and CO$_2$CH$_3$ systems, low doses of Ti still causes damage of CO$_2^-$ moieties as well as (CH$_2$)$_n$. For example, Ti$_x$C$_y$ complex forms in the CO$_2$H system as low at Ti doses as low as 0.13 nm, while there are still some CO$_2$H groups are unreacted. A plausible explanation for this observation is small Ti clusters are formed at some special area, resulting in this situation.

We find that most Ti atoms stay on top of all of the SAMs studied in this work (even the CH$_3$ surface). This is an advantage for application of metal substrate/organic thin film/top Ti contact sandwiches. However, a disadvantage is the formation of a Ti$_x$C$_y$ or Ti$_x$O$_y$ layer between Ti layer and organic layer (Figure 4-11b). So far, understanding of this Ti$_x$C$_y$ or Ti$_x$O$_y$ layer is poor. Some important parameters of this layer, such as thickness, component, conductivity, etc., are not known. We notice that Ti has been applied as a top contact metal for measurements of electronic properties of organic thin layers for many years, but the effect of this Ti$_x$C$_y$ (Ti$_x$O$_y$) layer is rarely discussed. Apparently, more studies are needed to fully understand the effect of this layer on measurements of electronic properties.

Besides Ti, Au is also a commonly used contact metal to prepare metal substrate/organic thin film/top metal contact sandwiches. It is interesting to compare the penetration behavior of Ti and Au on the different SAMs, especially the CH$_3$ SAM. Au atoms penetrate through the CH$_3$ film, and as a contrast, Ti atoms stay on top of the CH$_3$ film with weak penetration. During this process, chemical activity of the metal atoms seems to play the key role. Since the sticking coefficient of Au on the CH$_3$ surface is high, Au atoms reaching the CH$_3$ surface will stay in the system and cannot rebound back
to the vacuum. However, it is very difficult for them to find penetration pathways immediately. These Au atoms may move on the CH$_3$ surface for a long time until pathways appear just under them. As a contrast, most Ti atoms reaching the CH$_3$ surface are rebounded back to the vacuum at the beginning, and only those meeting some defect areas stay there and cannot move any more. Apparently, there should be a strong interaction between Ti atoms and these special areas. Thus, these Ti atoms stay on the surface and become nucleation centers. When more Ti atoms reach the surface they attach onto these nucleation centers and form 3-dimensional Ti clusters. Apparently these defects do exist when Au atoms reach the surface, but inert Au atoms pass them without stopping unless there is a pathway there.

4.4 Conclusions

In this paper, Ti is vapor-deposited on a number of alkanethiol SAMs with different surface organic functional groups, and ToF-SIMS is applied to characterize these systems. Most Ti atoms stay at the vacuum interface with weak penetration through the SAMs. The intensity of Ti/surface organic functional groups interactions can be ranked as Ti/CO$_2$H > Ti/CO$_2$CH$_3$ > Ti/CH$_3$. The intensity of Ti/surface organic functional groups interactions also affects the formation of clusters. Strong interactions lead to smooth overlayers (Ti on the CO$_2$H surface), and weak interactions lead to 3-dimensional clusters (Ti on the CH$_3$ surface). At low Ti doses, Ti atoms react with CO$_2$H and CO$_2$CH$_3$ groups, leading to CO$_2^-$ moieties and Ti$^{n+}$ ions at the interface. With more Ti atoms accumulating on the surface, the CO$_2^-$ moieties are gradually damaged, forming Ti$_x$O$_y$
and $\text{Ti}_x\text{C}_y$ complexes between the Ti overlayer and the organic layer. The sticking coefficient of vapor Ti atoms on the CH$_3$ surface is low at the beginning, and gradually increases with Ti accumulation. The CH$_3$ groups and (CH$_2$)$_n$ chain under the Ti clusters are found to be damaged to form $\text{Ti}_x\text{C}_y$ complex. Additionally, CO$_2$K layer is not an effective buffer layer to prevent organic layer from Ti destruction. Finally, since $\text{Ti}_x\text{C}_y$ ($\text{Ti}_x\text{O}_y$) complexes are formed between Ti and organic layer when Ti is vapor-deposited onto the organic surfaces as a contact metal, the effect of this $\text{Ti}_x\text{C}_y$ layer should be considered in the measurement of electronic properties of such metal substrate/organic thin film/top Ti contact sandwich structures.
4.5 References


(49) Zhu, Z.; Allara, D. L.; Winograd, N. *paper in preparation.*


Chapter 5

The Effect of Low Temperature on Au Penetration through SAMs

5.1 Introduction

Vapor-depositing Au on alkanethiol SAMs on Au substrates is a common way to prepare Au/SAM/Au top contact sandwiches, which has been used to test electronic properties of molecular electronic devices\textsuperscript{1-6}. However, it has been found that Au atoms penetrate through the alkanethiol SAMs at room temperature\textsuperscript{7-13}. Molecular dynamics simulation results show that the alkanethiol molecules can move on the Au substrates due to thermal energy, so that some temporary vacancies are generated for leakage of Au atom to the Au/S interface\textsuperscript{14,15}. Therefore low temperature, theoretically, could reduce Au atoms penetration through the alkanethiol SAMs. For example, Ag atoms are found to penetrate through C\textsubscript{17}CH\textsubscript{3} SAM at room temperature, but stay on top of the C\textsubscript{17}CH\textsubscript{3} SAM at 90K\textsuperscript{16,17}. Some research groups deposited Au on SAMs at low temperature to prepare metal substrate/organic thin film/top Au contact sandwich structures\textsuperscript{1-6,18,19}.

Although low-temperature preparation method is practical to prepare Au/SAM/Au sandwich structure, this system has not been well characterized. ToF-SIMS has proven a very useful technique to characterize similar systems\textsuperscript{7,20-28}. In this work, ToF-SIMS is applied to study the effect of temperature on the penetration behavior of Au atoms through SAMs. Our work aids in finding the optimum parameters for preparation of Au/SAM/Au sandwich structure.
Two series of experiments were done in this work. One is depositing 1.0 nm Au on C_{15}CH_{3}, C_{15}CO_{2}CH_{3} and C_{15}CO_{2}H SAM samples at different temperatures (from 90K to 295K), and comparing the SIMS spectra before and after Au deposition. The purpose of this experiment is to study the temperature effect on the behavior of Au atoms on SAMs. The other is cooling the C_{15}CH_{3}, C_{15}CO_{2}CH_{3}, C_{15}CO_{2}H, C_{16}OH and C_{16}OCH_{3} samples to 90 K, depositing 1.0 nm Au on them, and then gradually increasing the temperature, collecting SIMS spectra step by step. The purpose of this experiment is to study if the Au atoms, which stay at the vacuum interface, penetrate through the SAM with increasing temperature.

5.2 Experiment

SAM preparation, SIMS instrument, and details of metal deposition have been introduced in Chapter 2-4 and the appendix. Here, the low temperature control and experiment procedure are described.

The sample stages in the metal deposition chamber and the SIMS analysis chamber were cooled by liquid N\textsubscript{2}. The temperatures of the stages were monitored by two thermal couples, and they could be controlled by adjusting the flowing speed of liquid N\textsubscript{2}.

In experiment I, three samples (C_{15}CH_{3}, C_{15}CO_{2}CH_{3} and C_{15}CO_{2}H, freshly prepared) were immobilized on a sample block, and SIMS spectra were obtained at room temperature. Then the samples were cooled to a certain temperature, and SIMS spectra were taken again. The samples were transferred to the deposition chamber, which was cooled to the appropriate temperature. After 2-3 min (to ensure thermal equilibrium), 1.0
nm Au was deposited onto the samples at a rate of 0.01 nm/s. Then the samples were transferred to the SIMS analysis chamber (the temperature of sample stage in this chamber was set during the experiment) for acquisition of SIMS spectra. The following temperatures were employed: 95K, 123K, 150K, 188K, 222K, 260K, and 295K.

In experiment II, five samples ($C_{15}H_3$, $C_{15}CO_2H_3$, $C_{15}CO_2H$, $C_{16}OH$ and $C_{16}CH_3$, freshly prepared) were immobilized on a sample block, and SIMS spectra were obtained at room temperature. Then the samples were cooled to 90K, and SIMS spectra were taken again. The samples were transferred to the deposition chamber, in which the sample stage was already cooled to 90K. After 2-3 min (to ensure thermal equilibrium), 1.0 nm Au was deposited onto the samples at a rate of 0.01nm/s. Then the samples were transferred to SIMS analysis chamber, in which the sample stage temperature was kept at 90K, for acquisition of SIMS spectra. The samples were gradually warmed to 295K at a rate of 1.5 K/min. SIMS spectra were obtained approximately every 15 K. Due to limitation of time, only positive ion spectra were collected.

5.3 Result and Discussion

5.3.1 Experiment I

Very small differences were found between SIMS spectra from the SAM samples at room temperature and at low temperature, indicating that the effect of temperature on SIMS spectra is weak.
Figure 5-1, 5-2 and 5-3 show that the relationship between the temperature and normalized intensity of the characteristic peaks. The x-coordinate is the absolute temperature (K), and the y-coordinate is the normalized peak intensity, i.e., the ratio of peak intensity after 1.0 nm Au deposition \( (I_{\text{after}}) \) to peak intensity before Au deposition \( (I_{\text{before}}) \). For negative ion spectra (Figure 5-1A, 5-2A, 5-3A), at room temperature (295K), normalized intensities of most of the characteristic peaks is close to 1.0, indicating no significant structural change, that is to say, most Au atoms penetrate through the SAMs to form smooth buried layers under the SAMs. However, the normalized peak intensity gradually decreases with decreasing temperature, indicating that metal penetration becomes weaker and weaker. At 95K, most characteristic peaks become only 20-40% or even lower of their initial intensities. Our calculations show that 1.0 nm Au is about equal to four close-packed monolayers. If four smooth monolayers of Au stays on top of the organic layer, no S-related signal would be detected because the information depth of SIMS is shallow. Therefore, at low temperature, either metal penetration is still considerable, or metal clusters form on top of the SAMs with weak penetration. According to previous papers\(^{16,17}\) the later scenario is more plausible. However, no direct evidence shows that all metal atoms stay on top of the SAMs without any formation of filaments or “mushroom-like” structures at low temperatures. A STM or conducting probe AFM experiment is needed to answer this question.

Before conducting our experiment, we expected a critical temperature for each SAM, below which all Au atoms would stay on top of the SAM. H-bonds exist between organic molecules in the CO\(_2\)H SAM. If such a critical temperature exists, the CO\(_2\)H
Figure 5-1. The relationship between temperature and the normalized intensities for the C_{12}CH_{3} system. The x-coordinate is the absolute temperature (K), and the y-coordinate is the normalized peak intensity, i.e., the ratio of peak intensity after 1.0 nm Au deposition (I_{after}) to peak intensity before Au deposition (I_{before}). A: negative ion peaks; B: positive ion peaks.
Figure 5-2. The relationship between temperature and the normalized intensities for the C\textsubscript{15}CO\textsubscript{2}H system. The x-coordinate is the absolute temperature (K), and the y-coordinate is the normalized peak intensity, i.e., the ratio of peak intensity after 1.0 nm Au deposition (I\textsubscript{after}) to peak intensity before Au deposition (I\textsubscript{before}). A: negative ion peaks; B: positive ion peaks.
Figure 5-3. The relationship between temperature and the normalized intensities for the C_{12}CO_{2}CH_{3} system. The x-coordinate is the absolute temperature (K), and the y-coordinate is the normalized peak intensity, i.e., the ratio of peak intensity after 1.0 nm Au deposition (I_{after}) to peak intensity before Au deposition (I_{before}). A: negative ion peaks; B: positive ion peaks.
SAM should have a higher critical temperature value than the other two SAMs. Unfortunately, we could not determine such a temperature for CH₃ and CO₂H systems (for CO₂CH₃ system, 150K seems the critical temperature, but it may be just a coincidence in the error range of experiment). Since the distribution of metal atoms on top of the SAMs can also affect the intensity of the SIMS signals, it is very difficult to determine such critical temperatures by SIMS, even if they do exist.

The trend of positive ion spectra is not as regular as negative ion spectra (Figure 5-1B, 5-2B, 5-3B), but normalized peak intensities also decrease with the temperature decrease, in agreement with the results from the negative ion spectra. Molecular peaks and sulfur-atom related peaks are weak in the positive ion spectra. Therefore, negative ion spectra supply more valuable information in these studies.

### 5.3.2 Experiment II

Figure 5-4 shows the relationship between temperature and the intensities of some characteristic peaks for the C₁₅CO₂CH₃ system. H₃O⁺ and AuH₂O⁺ signals greatly increase after Au deposition, suggesting that H₂O molecules are condensed on the SAM surface with Au atoms at 90K. These two peaks are stable before 155K, but suddenly decrease to very low level after 155K, suggesting that over 155K, H₂O molecules rapidly evaporate from the vacuum interface. This temperature value is in agreement with the result from the previous documentation.

An interesting observation is H₂O⁺ peak and AuOH⁺ peak. The H₂O⁺ peak
Figure 5-4. The relationship between temperature and the intensities of some characteristic positive ion peaks from the C_{15}CO_{2}CH_{3} system. (1) Samples were cooled from 295K to 90K; (2) 1.0 nm of Au was deposited on the samples; (3) temperature was gradually increased from 90K to 295K with a rate of 1.5K/min, and SIMS spectra were obtained approximately every 15K.
appears after Au deposition, gradually increases before 155K, rapidly increases after 155K, gets to a summit at ~180K, then decreases to a very low level above 275K. The AuOH$^+$ peak shares a similar trend, but the summit is at about 212K, 30 K higher than H$_2$O$^+$ peak. The origin of these two peaks may be attributed to a surface adsorbed layer of H$_2$O molecules$^{31}$. It is reasonable to postulate that AuH$_2$O$^+$, AuOH$^+$, H$_2$O$^+$ and H$_3$O$^+$ are re-combination ions. The original ions are Au$^+$ and H$^+$, and they can combine with OH or H$_2$O neutral particles in the plume. However, when multi-layer H$_2$O molecules exist on the surface, the major neutral particle in the plume is H$_2$O, but if only a very thin layer of H$_2$O molecules exist, the major neutral particles are HO.

CO$_2$CH$_3^+$ ions are found to greatly decrease after Au deposition, indicating that Au and H$_2$O layer stays on top of the SAM. Before 155K, this structure is relatively stable, but after 155K, the CO$_2$CH$_3^+$ signal immediately jumps up when multi-layer of H$_2$O molecules leave the surface, and then gradually increases with temperature further increasing. Since the recovery of the CO$_2$CH$_3^+$ peak associated with H$_2$O leaving, it is difficult to say whether or not Au penetrates through the SAM with increasing temperature. However, since the final spectrum is very similar to the initial spectrum, the penetration of Au is likely.

In this experiment, it is a pity that I did not collect negative ion spectra. From the results of experiment I, the negative ion spectra are more regular than the positive ion spectra. The reason is that experiment II was done before experiment I. Therefore, a repeat of the experiment II may be necessary.

The results from the CH$_3$, CO$_2$H, OH and OCH$_3$ systems are very similar to the results from the CO$_2$CH$_3$ system. Therefore, the data of these systems are not shown here.
5.4 Summary and future work

Low temperature does reduce Au penetrate through the alkanethiol SAMs on Au substrate, but it is difficult to determine whether or not all Au atoms stay on top of the SAMs. STM or conducting AFM may be able to answer this question. We also find that H₂O molecules stay with Au atoms on top of the SAMs if the samples are cooled below 155K. Although the H₂O molecules can escape from the surface when the samples are warmed to room temperature, the effect of the H₂O molecules on the structure of Au overlayers is not clear.

From these results, it is plausible that by depositing enough Au on top of the SAMs at low temperature, continuous metal overlayers would form at the vacuum interface, and it is interesting to know the structure of such samples when they are warmed to room temperature. An ideal scenario would be that the top Au atoms form a continuous Au film on top of the SAM with weak penetration. We plan to study this system in the near future.
5.5 References:


(29) It is difficult to remove all H$_2$O molecules in our vacuum system. In the experiment, the base pressure in the deposition chamber is generally $2-3 \times 10^{-9}$ torr and increases to $<10^{-7}$ torr during Au deposition. To reduce the condensation of H$_2$O molecules, we baked the deposition chamber for three days and got to $5 \times 10^{-10}$ torr before metal deposition, and residue gas detector showed that only 5% of residue gas was H$_2$O. Unfortunately, during Au deposition, the pressure in the metal deposition chamber increase to $2 \times 10^{-8}$ torr, and residue gas detector showed that 50% of the residue gas was H$_2$O. Metal deposition time was about 2 min, but the samples exposed in $2 \times 10^{-8}$ torr condition for about 5-6 min altogether during experiment. Therefore, about three layers of H$_2$O stayed on top of the SAM if the condensation coefficient was 100%. Compared with the results without baking, the H$_2$O-related peaks in SIMS spectra greatly decrease, but totally removing H$_2$O molecules is difficult.

(31) The existence of the surface layer of H$_2$O may be related to the Au clusters on top of the SAMs. The surface of Au clusters is very active and prefers to adsorb molecules especially H$_2$O molecules in the system (Need an experiment to support this speculation).
Chapter 6

Conclusions and Future works

6.1 Metal behavior on SAMs

6.1.1 Chemical reactions at top metal contact/SAM interfaces

Au is an inert metal and no chemical reactions are found between Au atoms and organic functional groups. K and Ti are active metals and they react with a number of surface organic functional groups. Ti is especially active and is able to damage \((\text{CH}_2)_n\) chains.

In this thesis, five surface organic functional groups are exposed under the K vapor. Their reactivity can be ranked as \(\text{CO}_2\text{H} > \text{CO}_2\text{CH}_3 > \text{OH} > \text{OCH}_3 > \text{CH}_3\). K atoms are found to react with active surface organic functional groups, \(\text{CO}_2\text{H}, \text{CO}_2\text{CH}_3\) and \(\text{OH}\), to form \(\text{CO}_2\text{K}\) or \(\text{OK}\) moieties. \(\text{OCH}_3\) groups only form complexes with K atoms and no significant chemical reactions are observed. Very weak K/\(\text{CH}_3\) interactions are found. All these results are consistent with the results of traditional organic reactions.

Ti is such an active metal that it not only reacts with surface organic functional groups but also damages them as well as \((\text{CH}_2)_n\) chains. On the \(\text{CO}_2\text{H}\) and \(\text{CO}_2\text{CH}_3\) surfaces, Ti atoms firstly react with them to form \(\text{CO}_2^-\) moieties, and with more Ti doses, the \(\text{CO}_2^-\) moieties, as well as \((\text{CH}_2)_n\) chains, are damaged to form \(\text{Ti}_x\text{O}_y\) and \(\text{Ti}_x\text{C}_y\)
complexes. Although Ti/CH$_3$ interactions are weak, Ti atoms stay on top of the CH$_3$ film, and damage CH$_3$ groups as well as (CH$_2$)$_n$ chains to form Ti$_x$C$_y$ complex.

### 6.1.2 Metal penetration through the SAMs

At room temperature, if deposition rates are fixed, metal penetration is related to two major factors. One is the interactions between metal atoms and surface organic functional groups; the other is intermolecular interactions. If these two interactions are all weak, metal atoms will easily penetrate through the SAMs, for example, Au on CH$_3$ surface. If one of them is a little stronger, some of metal atoms stay on top of the SAMs, with considerable penetration, for example, Au on CO$_2$H surface (H-bond between film molecules) or Al on OCH$_3$ surface (Al-O interactions). If one of them is strong, most of metal atoms stay on top of the SAM, for example, Au on CO$_2$K surface (strong intermolecular interactions) or K on CO$_2$CH$_3$ surface (strong metal/surface organic functional groups interactions). However, if metal/surface organic functional groups interactions are too strong, although metal penetration is pretty weak, organic molecules are damaged, for example, Ti on CO$_2$H SAM.

It is found that decreasing sample temperature does reduce metal penetration through the SAMs. However, if the temperature is below a certain value (for example, 155K at 10$^{-9}$-10$^{-8}$ torr), H$_2$O molecules will condense on the sample surface, and the effect of these H$_2$O molecules on structure of metal overlayers is not clear so far.
6.1.3 Clusters formation and sticking co-efficient

If metal atoms stay on top of the SAM, the metal/surface organic functional group interactions determine the formation of clusters or smooth overlayers. Weak interactions lead to 3-dimensional clusters and strong interactions lead to smooth overlayers. For example, Ti forms clusters on top of the CH$_3$ surface, but forms smooth layers on the CO$_2$H surface. Intermediate situations also exist, for example, Ti on the CO$_2$CH$_3$ surface, in which Ti overlayers on the CO$_2$CH$_3$ surface are not as smooth as Ti overlayers on the CO$_2$H surface, but Ti does not form big clusters like Ti/CH$_3$ system.

An interesting observation is the relationship between sticking coefficient and metal atom/surface organic functional group interactions. For low atomic mass metals such as K, Ti, Al, weak interactions correspond to a low sticking co-efficient (for example, they are on the CH$_3$ surface) and strong interactions correspond to a high sticking coefficient (for example, any of them on the CO$_2$H surface). As an example, the sticking coefficient of Al atoms on different surfaces is shown in Figure 6-1. However, for high atomic mass metals such as Au, the sticking coefficient is always 100% even if Au/surface organic functional group interactions are very weak. It is a little difficult to clearly explain this observation, but one possible reason is that high mass atoms have relatively large momentum but low velocity and they interact with surface longer than low mass atoms, and lose energies and can not escape from the surfaces.
Figure 6-1. Sticking coefficient of Al atoms on Al metal surface (square), CO$_2$H (down triangle), CO$_2$CH$_3$ (up triangle), OH (crossing), OCH$_3$ (diamond) and CH$_3$ (circle). Here, Al dose ($I_{ref}$) is the thickness value from the reference QCM crystals (rough Au surface). The sticking coefficient is the ratio of the thickness value from the SAM-modified QCM crystals ($I$) to the thickness value from the reference QCM crystals ($I_{ref}$). A previous paper postulates that the sticking coefficient of Al atoms on the CH$_3$ surface is 100%$^1$, and that is not seen here.
6.1.4 Damage effect of Ti atoms

Ti is so active that it not only reacts with surface organic functional groups but also damages them as well as the \((\text{CH}_2)_n\) chains. As a comparison, K is also an active metal but it only reacts with surface organic functional groups. This observation may be explained by two possible reasons. One is Ti can form small diameter, high charge number ions, which is more active than large diameter, low charge number \(\text{K}^+\) ions. Another reason is Ti atoms can form metal-metal bonds between them, and then cooperation of Ti atoms can destroy C-H bond, C-O bond or C-C bond easily.

6.2 Useful tips for metal deposition process

K proves to be a safe and useful reagent to modify SAM surfaces. Additionally, an interesting result is that the \(\text{CO}_2\text{H}\) film prepared by K modification and water rinse is more ordered than the freshly prepared \(\text{CO}_2\text{H}\) film.

Enhancing intermolecular interactions is an effective way to reduce penetration of inert metal atoms through the SAMs. However, due to weak interaction between metal atoms and surface organic functional groups, inert metals form islands on top of the film rather than smooth layers.

Ti is such an active metal that it can damage even inert organic surface such as \(\text{CH}_3\) surface. However, the penetration of Ti atoms through the SAMs is low. Additionally, active surface organic functional groups result in smooth Ti layers on top of
the organic thin films. This point may be useful in preparation of Ti overlayers on top of the organic thin films.

### 6.3 How to use SIMS to detect structural information of metal/SAM interfaces

To understand the structure of top metal contact/SAM interfaces, the questions that should be answered include: chemical reactions between metal atoms and surface organic functional groups, penetration of metal atoms through the SAMs, growth modes of metal overlayers on top of the SAMs, and damage of surface organic functional groups and \((\text{CH}_2)_n\) chains. In this thesis, ToF-SIMS is applied to investigate the behavior of vapor-deposited K, Au and Ti atoms on several alkanethiol SAMs. Via these sample systems, we demonstrate how to use ToF-SIMS to determine chemical reactions, penetration, cluster formation and damage.

It is found that appearance of new peaks and disappearance of initial characteristic peaks may indicate the occurrence of chemical reactions. One example is K/CO\(_2\)CH\(_3\) system in Chapter 2. The S(\(\text{CH}_2\))\(_{15}\)CO\(_2\)CH\(_3\)\(^-\) peak increases at low K doses because accumulation of K atoms in the system results in a decrease of the surface work function. This peak dramatically decreases after 0.63 nm of K and gets to nearly noise level at 0.83 nm. At the same time, the S(\(\text{CH}_2\))\(_{15}\)CO\(_2\)K\(^-\) peak continuously increases. Combining these data, we believe that K reacts with CO\(_2\)CH\(_3\) groups to form CO\(_2\)K moieties. In addition, OCH\(_3\), HAU(S(\(\text{CH}_2\))\(_{15}\)CO\(_2\)CH\(_3\)\(^-\) and Au[S(\(\text{CH}_2\))\(_{15}\)CO\(_2\)CH\(_3\)]\(_2\)\(^-\) peaks also decrease to nearly
noise level after 0.83 nm dose, indicating most of CO\textsubscript{2}CH\textsubscript{3} groups react with K atoms to form CO\textsubscript{2}K moieties.

The relationship between metal dose and intensity of characteristic peaks can be applied to determine metal penetration through the SAMs. In Chapter 3, when Au atoms are deposited on the CO\textsubscript{2}CH\textsubscript{3} film at room temperature, CO\textsubscript{2}CH\textsubscript{3}\textsuperscript{+} peak remains constant even after 4.0 nm Au deposition, implying that most of the Au atoms continuously penetrate through the SAM. As a comparison, when Au atoms are deposited on 0.4 nm K modified-CO\textsubscript{2}CH\textsubscript{3} SAM, only 2.0 nm of Au diminishes the CO\textsubscript{2}CH\textsubscript{3}\textsuperscript{+} peak to noise level, indicating that most of Au atoms stay on top of the film (Chapter 2 shows that after 0.4 nm of K deposition, there are still 40-50\% of CO\textsubscript{2}CH\textsubscript{3} groups remain).

The relationship between metal dose and intensity of characteristic peaks can also be applied to determine metal growth mode on top of the SAMs. In Chapter 4, when Ti is deposited on the CO\textsubscript{2}H and CH\textsubscript{3} SAMs, most Ti atoms are found to stay on top of the SAM. It is found that 0.25 nm of Ti quenches the Au\textsubscript{2}S(CH\textsubscript{2})\textsubscript{15}CO\textsubscript{2}H\textsuperscript{-} peak, but after 2.22 nm of Ti deposition, Au\textsubscript{2}S(CH\textsubscript{2})\textsubscript{15}CH\textsubscript{3}\textsuperscript{-} peak is still clear. Our calculation shows that the thickness of a monolayer of close-packed Ti atoms is about 0.26 nm. Therefore, the above data indicate that Ti forms a smooth overlayer on top of the CO\textsubscript{2}H surface but forms 3-dimensional clusters on top of the CH\textsubscript{3} surface.

It has been found that Ti damages the surface organic functional groups as well as (CH\textsubscript{2})\textsubscript{n} chains. In Chapter 4, we use a characteristic peak, TiC\textsuperscript{+}, as an indicator of destruction. The reason is that the Ti\textsubscript{x}C\textsubscript{y} complex is a damage product, which is the source of Ti-C cluster.
Metal overlayers on top of the SAMs affect the signal intensities. For example, since the information depth of static SIMS is shallow, clusters of organic species cannot escape from the system if 1-2 metal overlayers totally cover the sample. Therefore, using chemical etching to remove metal overlayers is a complementary way to get more useful information. An example is Ti/CO$_2$CH$_3$ system in Chapter 4. 0.60 nm of Ti eliminates CO$_2$CH$_3^+$ signal. But after the Ti overlayers are removed by 5% HF aqueous solution, CO$_2$CH$_3^+$ peak is still clear (about 20% of the initial intensity), indicating that a small fraction of CO$_2$CH$_3$ groups are still untouched.

6.4 Future work

Although SIMS is a powerful technique to characterize the metal/SAM interfaces, it has some limits. For example, it cannot supply topographic information. At the same time, if some filaments form between substrates and top metal overlayers, SIMS cannot determine it. STM/AFM are good tools to provide this information. Therefore, using STM/AFM to characterize the metal/SAM systems studied in this thesis is necessary to fully understanding the structure of metal/SAM interfaces. Some systems have been studied by STM$^2$, but more data are needed. One example is the Ti/SAM system. We know that Ti damages surface organic functional groups as well as (CH$_2$)$_n$ chains, but with weak penetration. I want to use STM to study the destruction depth of Ti overlayers on different surfaces. In detail, a series of different length SAMs, S(CH$_2$)$_n$X (n = 10-20), can be prepared, and then 5 nm of Ti could be deposited on them, and the STM will be applied to detect a short between top metal contact and substrates.
6.5 References


Appendix A

Some Experiment Details

(1) Metal Deposition Chamber

Since many delicate metal depositions would be performed in my research, a suitable metal deposition chamber should be constructed. A previous deposition chamber was designed and constructed by Brendan Haynie (PhD thesis, Penn State University, 2003), which had some disadvantages, so I redesigned and reconstructed the deposition chamber.

A schematic illustration of the structure of my metal deposition chamber is shown in Figure 1. This chamber is pumped by a turbo-pump of the preparation chamber of the BIOTOF2 instrument. There is a gate valve (2) between these two chambers. The sample can be transferred into the deposition chamber and stay on the sample stage (3) via a transfer arm (1). The sample stage has a cooling line (6) so that liquid N₂ or hot air can pass through the line to cool or heat the sample stage. A thermal couple (7) is immobilized on top of the sample stage to monitor the temperature of the sample. The metal source (15) is on top of the deposition chamber and the distance between the metal source and the sample surface is about 50 cm. A quartz crystal microbalance (5) is installed on the sample stage but does not shade the sample. The distance between the metal source and surface of the quartz crystal is about 47 cm. A removable shutter (8) is
Figure 1. Schematic illustration of the structure of the metal deposition chamber.
installed between the metal source and the sample stage. Additionally, a vacuum gauge (14) is installed to detect the pressure in the chamber; a video camera (12) is installed on top of the chamber and through a glass window (11) to monitor the deposition chamber. A vent valve (13) is installed so that the chamber can be vented. A stainless steal shade (10) is installed on top and side of the metal source to prevent vapor metal atoms from covering the glass window.

A photo of the deposition chamber is shown in figure 2. The valve (l) is installed between the preparation chamber and the deposition chamber. A transfer arm (h) is used to transfer a sample block between these two chambers. A video camera (i) is installed on top of the deposition chamber, and through the glass window (j) it can monitor the situation in the deposition chamber. A vent valve (k) is installed below the glass window (j). The deposition chamber has (a), (b), (c), (d), (e), (f), and (g) seven 6” flanges, and different parts can be installed onto these positions.

As the initial design, a glass window was installed at position (a); the sample stage was installed at position (b); QCM was installed at position (c); a thermal couple was installed at position (d); the removable shutter was installed at position (e); a vacuum gauge was installed at position (f); and the metal source was installed at position (g). After some time, I found that the pressure measured from position (f) was always about 1.5 to 2 times of the value measured from the preparation chamber. So I removed the vacuum gauge from the position (f), and installed another metal source there. Thus, two kinds of metals could be deposited simultaneously.

Generally, metal slugs (Au, Ag, Al, Ti, and so on) are put into a tungsten basket and DC current is applied to the tungsten basket to heat the metal slugs to metal vapor.
Metal deposition rate can be controlled by the heating current. In normal conditions, the current is about 30-60 ampere. K and Na vapor is generated from special getters (bought from SAES), which can be directly heated by 6-10 ampere current.

If the metal source is installed at (f) or (g) position (figure 2), the distance between the metal source and the samples is about 50 cm. This distance is suitable for fine deposition (from sub-angstrom to about 5 nm). If a high dose of metal overlayers are needed (>5nm), this distance is too long. So the metal source can be installed at (e) position. In this way, the distance between metal source and the samples is about 25 cm, and the metal deposition efficiency becomes much higher. Note that: to prevent the metal vapor from covering the glass windows or contaminating another metal source in the system, a stainless steel shade is attached on top of each metal source.

The steps to change a metal source: [1] close the valve (l); [2] vent the system through the vent valve (k); [3] remove the metal source and then replace it; [4] re-install the metal source; [5] pump the system via the vent valve (k) by a mechanic pump for 5 min; [6] close the vent valve (k); [7] carefully and slightly open the valve (l), check the pressure of the preparation chamber, make the pressure near $5 \times 10^{-4}$ torr, wait for 5 min; [8] if the pressure of preparation chamber is in $10^{-5}$ to $10^{-4}$ torr range or even lower, totally open valve (l); [9] wait for several hours, the pressure should be in a $10^{-8}$ to $10^{-7}$ torr range. If a higher vacuum degree is needed, the system should be pumped overnight or baked. The pressure of the system can be roughly estimated by the position of the handle of the removable shutter (Figure 2 (m) position). Because of the spring effect of the bellow, the handle will be sucked in if the pressure in system is lower than 1 atm.
Figure 2. A photo of the metal deposition chamber.
and be pushed out if the pressure in the system is higher than 1 atm. The balance position is labeled (Figure 2 (m) position).

Controlling the metal deposition rate is a pure experience matter. A lot of practice is needed to get the optimum parameters (mainly current).

The experiment of testing sticking coefficient of metals on different SAM surfaces is also performed in this deposition chamber. Figure 2 shows this situation. Position (a) is the removable shutter; position (b) is the objective QCM; position (c) is the reference QCM; and position (g) is the metal source. During the experiment, two QCM heads are exposed under the metal vapor simultaneously, and two QCM monitors are used to monitor the metal thickness on two surfaces separately.

(2) Super Piranha solution:

The reproducibility of SIMS spectra of SAM samples is very important. The procedure for the preparation of alkanethiol SAMs on Au substrates is well-established [see references in Chapter 2]. In brief, Au is deposited on a Si substrate via a Ti or Cr adhesion layer, and the freshly prepared Au substrate is immersed into 1mM corresponding thiol solutions for 1-2 days. Then the samples can be taken out from the solution and rinsed by a relevant solvent and dried by flowing N2. Generally, the reproducibility of such samples is pretty good. However, in my experiments, sometimes some Cu⁺ or Ag⁺ contamination was found, and the reason is still unknown. At the same time, it is not convenient to deposit Au every time. Therefore, a reliable method is necessary to clean the Au substrates, especially for those substrates exposed in air for
some time. A piranha solution procedure (3:7 30% H₂O₂ vs 98% H₂SO₄, 90 °C for 5 min) has been used for a long time, but I find that it is not effective or convenient enough. I developed a new method to clean Au substrates, named “super piranha solution”.

Experimental details are: [1] 5 ml 30% H₂O₂ is put into a 50 ml beaker; [2] Au substrates are immersed into H₂O₂; [3] 0.5 ml 69% HNO₃ is added into the beaker; [4] 98% H₂SO₄ is added into the beaker drop by drop; [5] after about 6-7 ml H₂SO₄ is added into beaker, the solution begins to boil; [6] after a little more H₂SO₄ is added into the beaker, the solution in beaker begins to vigorously boil, and brown gas appears; [7] when all brown gas is gone, the solution stops boiling; [8] wait for about 2 min, take the Au substrates out and rinse them by ultra-pure water 3-4 times, the sample surface should be very hydrophilic, indicating that the sample surface is clean; [9] rinse the substrates by corresponding solvent and put them into thiol solution.

Experimental results show that the reproducibility of SIMS spectra of the SAM samples is excellent, and no Cu⁺ or Ag⁺ contamination is found.

Two tips should be mentioned here: (1) the reaction is very vigorous, and the brown gas may be poisonous NO₂, so the volume of solution should not be large, and the experiment should be done in a fume hood; (2) AFM results show that the surface of the Au substrates after treatment of super piranha solution is rougher (rms ~ 2.0-2.5 nm) than those before treatment (rms ~ 1.5 nm).
VITA

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