

# Chemistry of metal atoms reacting with alkanethiol self-assembled monolayers

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## Abstract

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is utilized to investigate the behavior of vapor-deposited K, Au and Ti atoms on several alkanethiol self-assembled monolayers (SAM). The goals are 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 of organic molecules. It is found that appearance of new characteristic peaks and disappearance of initial peaks may indicate chemical reactions or decomposition of organic molecules. The relationship between metal dose and intensity of surface organic functional group-related peaks provides information about penetration or cluster-formation of metal atoms. In addition, removing the metal overlayers by chemical etching and then characterizing samples again is a complementary approach that can reveal valuable information about the location of the metal atoms. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** ToF-SIMS; SAM; Metal deposition; Interface

## 1. Introduction

The structure of metal/alkanethiol self-assembled monolayers (SAM) interfaces is interesting for several reasons. One of them is that this system can be used as a model system to understand metal/polymer interfaces [1]. Polymer surfaces are complex and composed of a number of different organic functional groups. In contrast, alkanethiol SAMs have an ordered structure and the surface organic functional groups can be controlled [2]. Another motivation comes from the field of molecular electronics [3], where functional molecules are employed as a substitute for present silicon-based circuits. Many of these molecules have been reported, and one way to test their efficiency is to fabricate a metal substrate/organic thin film/metal top contact “sandwich” structure [4]. The functional molecules can be immobilized on metal substrates by self-assembly or by the Langmuir–Blodgett (LB) film technique, and the top metal contact can be prepared by metal evaporation. The structure of top metal contact/organic thin film interfaces certainly influences electronic properties, and characterization

of these “sandwich” structures is an essential part of building successful devices.

To understand the structure of metal/SAM interfaces, it is important to monitor 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. We have utilized time-of-flight secondary ion mass spectrometry (ToF-SIMS) to characterize the metal/alkanethiol SAM interfaces for several years [5–8], and it has proven to be an excellent technique. In this paper, ToF-SIMS is applied to investigate the behavior of vapor-deposited K, Au and Ti atoms on several alkanethiol SAMs. With these systems, we demonstrate the power of ToF-SIMS to obtain detailed information about the surface chemistry.

## 2. Experimental

The ToF-SIMS instrument has been described elsewhere [5,6]. The primary ions are 15 keV  $\text{Ga}^+$  ions, and the beam is rastered over a  $300 \mu\text{m} \times 300 \mu\text{m}$  area. The total ion dose is less than  $10^{12}$  ions/cm<sup>2</sup> in all measurements. Metal deposition is performed in an attached vacuum chamber. The K source is a dispenser (SAES getters), and Ti and Au slugs (Aldrich, 99.99%)

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are evaporated from heated tungsten baskets. All sources are located about 50 cm vertically above the SAM samples. Metal deposition rates are controlled to be 0.001, 0.002 and 0.01 nm/s for K, Ti and Au, respectively. The resulting metal thickness is monitored by a quartz crystal microbalance (Maxtek TM400 controller, 6 MHz Sycon crystal head).

Alkanethiol SAMs of  $S(\text{CH}_2)_{15}\text{X}$  ( $\text{X} = -\text{CO}_2\text{H}$ ,  $-\text{CO}_2\text{CH}_3$  and  $-\text{CH}_3$ ) on Au coated Si wafers were prepared and characterized using previously published procedures [5,6]. SIMS spectra of freshly prepared monolayers were taken, and the samples were transferred under vacuum to the deposition chamber, where a certain dose of metal atoms was deposited on the samples. After deposition, the samples were transferred back to the analysis chamber to acquire SIMS spectra.

### 3. Results and discussion

The negative ion ToF-SIMS spectra of K deposited at different doses onto the  $\text{CO}_2\text{CH}_3$  film are shown in Fig. 1. The  $S(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3^-$  peak increases at low K dose since accumulation of K atoms results in a decrease of the surface work function [9]. This peak dramatically decreases after 0.63 nm of K and approaches the background level after 0.83 nm of deposition. At the same time, the  $S(\text{CH}_2)_{15}\text{CO}_2\text{K}^-$  peak continuously increases. By combining these data, we believe that K reacts with  $\text{CO}_2\text{CH}_3$  groups to form  $\text{CO}_2\text{K}$  moieties. In addition, the  $\text{OCH}_3^-$ ,  $\text{HAuS}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3^-$  and  $\text{Au}(\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3)_2^-$  peaks also decrease to background after a dose of 0.83 nm, indicating most of the  $\text{CO}_2\text{CH}_3$  groups react with K atoms.

To be sure that all  $\text{CO}_2\text{CH}_3$  groups have reacted with K atoms to form  $\text{CO}_2\text{K}$ , 1.0 nm of K is deposited onto a  $\text{CO}_2\text{CH}_3$  sample, and then the sample is taken from the vacuum and rinsed with  $\text{H}_2\text{O}$ . The spectra of this sample are very similar to the spectra from a freshly prepared  $\text{CO}_2\text{H}$  film, and no  $\text{CO}_2\text{CH}_3$  group-related peaks are detected. This result certainly suggests that nearly all  $\text{CO}_2\text{CH}_3$  groups have reacted with K atoms to form  $\text{CO}_2\text{K}$  groups, and then  $\text{CO}_2\text{K}$  groups react with  $\text{H}_2\text{O}$  molecules to form  $\text{CO}_2\text{H}$  groups. From the above two

examples, we conclude that the appearance of new peaks and the disappearance of initial characteristic peaks may indicate the occurrence of chemical reactions.

The appearance of new characteristic peaks may also indicate damage to the surface organic functional groups and the  $(\text{CH}_2)_n$  chain. For example, when Ti is deposited on SAMs, the  $\text{TiC}^+$  peak is utilized as an indicator of this damage [10–12]. The reason is that the  $\text{Ti}_x\text{C}_y$  complex is one of the reaction products and is the source of the Ti–C cluster.

The relationship between metal dose and intensity of characteristic peaks can be utilized to determine metal penetration through the SAMs. For example, when Au atoms are deposited on a  $\text{CO}_2\text{CH}_3$  film at room temperature, the  $\text{CO}_2\text{CH}_3^+$  peak remains constant even after 4.0 nm of Au deposition, implying that most of the Au atoms continuously penetrate through the SAM, although formation of filaments and big clusters cannot be totally excluded. By comparison, when Au atoms are deposited on a 0.4 nm K modified- $\text{CO}_2\text{CH}_3$  SAM, only 2.0 nm of Au attenuates the  $\text{CO}_2\text{CH}_3^+$  peak to background, indicating that most of the Au atoms stay on top of the film. It is interesting that after 0.4 nm of K deposition, 40–50% of the  $\text{CO}_2\text{CH}_3$  groups remain unreacted [10].

The relationship between metal dose and intensity of characteristic peaks can also be used to determine the metal film growth mode on top of the SAMs. For example, when Ti is deposited on the  $\text{CO}_2\text{H}$  and  $\text{CH}_3$  SAMs, most Ti atoms are found to stay on top of the SAM while the surface organic functional groups and partial  $(\text{CH}_2)_n$  chain are damaged [10]. As shown in Fig. 2, 0.25 nm of Ti quenches the  $\text{Au}_2\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}^-$  peak, but after 2.22 nm of Ti deposition, the  $\text{Au}_2\text{S}(\text{CH}_2)_{15}\text{CH}_3^-$  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  $\text{CO}_2\text{H}$  surface but forms three-dimensional clusters on top of the  $\text{CH}_3$  surface.

Metal overlayers on top of the SAMs affect the signal intensities. For example, since the information depth of static SIMS is on the order of a monolayer thickness, clusters of organic species cannot escape from the system if 1–2 metal

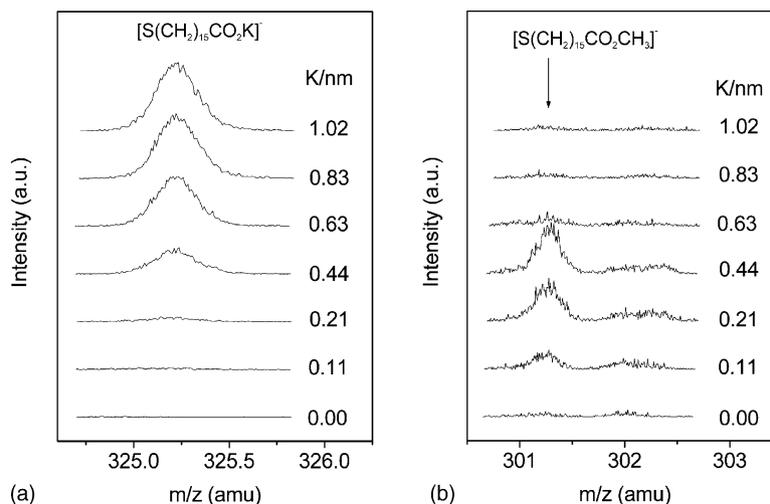


Fig. 1.  $S(\text{CH}_2)_{15}\text{CO}_2\text{K}^-$  and  $S(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3^-$  peaks from the negative ion spectra of a  $\text{CO}_2\text{CH}_3$  film with increasing amounts of K dose.

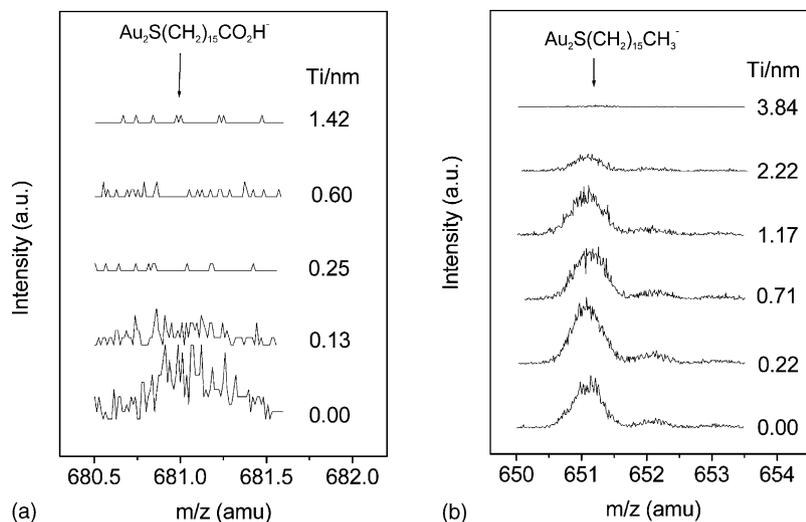


Fig. 2.  $\text{Au}_2\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}^-$  peak from a  $\text{CO}_2\text{H}$  film and  $\text{Au}_2\text{S}(\text{CH}_2)_{15}\text{CH}_3^-$  peak from a  $\text{CH}_3$  film with increasing amounts of Ti dose.

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 the  $\text{Ti}/\text{CO}_2\text{CH}_3$  system, where deposition of 0.60 nm of Ti eliminates the  $\text{CO}_2\text{CH}_3^+$  signal. But after the Ti overlayers are removed by 5% HF aqueous solution, the  $\text{CO}_2\text{CH}_3^+$  peak is observed with 20% of the initial intensity, indicating that there is still a small fraction of  $\text{CO}_2\text{CH}_3$  groups that are unreacted.

#### 4. Summary

ToF-SIMS is applied to investigate the behavior of vapor-deposited K, Au and Ti atoms on several alkanethiol SAMs. It is found that appearance of new characteristic peaks and disappearance of initial peaks may indicate chemical reactions or decomposition 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 the samples again is a complementary method that can supply useful information.

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