



Static SIMS study of the behavior of K atoms on $-\text{CH}_3$, $-\text{CO}_2\text{H}$ and $-\text{CO}_2\text{CH}_3$ terminated self-assembled monolayers

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Abstract

Time-of-flight secondary ion mass spectroscopy has proven to be a very powerful tool in the study of the interaction of metal atoms with organic thin films since analysis of the emitted molecular cluster ions provide clear information about the presence of chemical reactions, metal penetration and metal nucleation. In this work, this approach is employed to examine the behavior of K atoms evaporated onto $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$, $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ self-assembled monolayers on Au substrates. On the $-\text{CH}_3$ surface, no chemical reaction is observed, and the sticking probability of K atoms is quite low. However, we find that K atoms react with $-\text{CO}_2\text{H}$ and $-\text{CO}_2\text{CH}_3$ groups, forming $-\text{CO}_2\text{K}$ moieties at the vacuum interface, but do not react with the $-(\text{CH}_2)_n-$ backbone. Additional exposure of K to the system results in K remaining at the vacuum interface, not penetrating through the organic layer. The results imply that the CO_2K may act as a possible buffer layer to prevent chemical reactions when other types of metal atoms are employed.

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1. Introduction

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is 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 [1–3]. For example, using alkanethiol self-assembled monolayers (SAMs), the presence of metal–surface organic functional group cluster ions indicate at least a fraction of

deposited metal atoms stay at the vacuum interface and the detection of metal- SH_2^+ cluster ions are an indicator of metal penetration [3].

Our interest in studying metal/organic functional group interactions is aimed towards developing contacts between organic molecules and atomic metal electrodes. Well-defined contacts are necessary for development of molecular electronic devices [4,5]. Moreover, there is a need for better understanding of these interactions as they apply to polymer coatings and polymer electronic devices. In the last decade, many metal/SAM studies have been published elucidating a range of chemical reactivities with only some systems yielding reliable electrical contacts [6]. For example, it has been found that metal atoms penetrate

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through the Au substrate alkanethiolate SAMs if metal/organic functional group interactions are weak [1]. This is a serious technical impediment to fabrication of SAM-based nano-devices. Here we show that alkali metal atoms, with their inherent ionic character, may be employed as a possible buffer layer to allow otherwise reactive metals to act as viable metal contacts. The data suggest that for K deposition on carboxylic acid and ester terminated alkanethiols that this ionic character dominates the van der Waals interactions between molecules, blocking penetration of subsequently deposited species. In general, we illustrate the power of the ToF-SIMS approach for characterizing such complex structures.

2. Experimental

A custom-designed ToF-SIMS instrument was used in this paper, and the details of the instrument have been described elsewhere [7]. The primary ions are 15 keV 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^2 in all measurements. Atomic K was deposited on top of the samples in a deposition chamber using a dispenser (SAES getters), which was located about 45 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, 6 MHz Sycon crystal head).

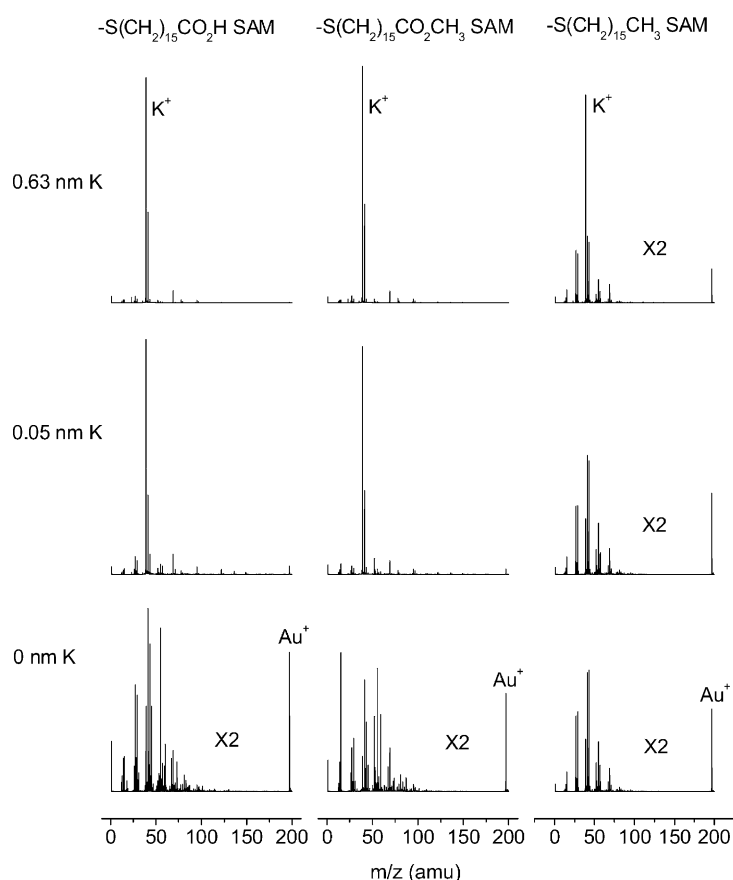


Fig. 1. Positive ion spectra of the $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$, $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ monolayers before and after 0.05 and 0.63 nm K deposition. From left to right, $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$, $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$, and $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$; from bottom to top, original samples, after 0.05 nm K deposition, and after 0.63 nm K deposition.

Self-assembled alkanethiolate monolayers of $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$, $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ on Au coated Si wafers were prepared and characterized using previously published procedures [8]. SIMS spectra of freshly prepared monolayers were taken, and then the samples were transferred under vacuum to the 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. After SIMS analysis, the samples were redosed with additional K. This process was repeated for total K doses of 0.05, 0.15, 0.39, 0.63 and 0.93 nm. In another experiment, 1.2 nm K was directly deposited on the samples, which were then removed from vacuum and rinsed by millipore water (18.2 M Ω cm). After drying, they were put back into the analysis chamber.

3. Results and discussion

The positive ion spectra of $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$, $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ monolayers before and after K deposition are shown in Fig. 1. We find that after 0.05 nm of K deposition, the $^{39}\text{K}^+$ peak dominates the spectra of $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ monolayers. With additional deposition, the relative intensity of the $^{39}\text{K}^+$ peak becomes stronger. However, the $^{39}\text{K}^+$ peak in the spectrum of the $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$ monolayer is relatively weak even after 0.63 nm K deposition. This observation indicates that the sticking probability of K atoms on the $-\text{CH}_3$ surface is very low. When comparing the K^+ peak intensities from the various samples, it is found that the sticking probability of K atoms on the $-\text{CH}_3$ surface is no more than 2% of that on the $-\text{CO}_2\text{H}$ or $-\text{CO}_2\text{CH}_3$ surface.

With K deposition on the $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$ surface, K^+ peaks increase and all original peaks decrease, but relative intensities between the original peaks change only slightly. At the same time, characteristic negative ion peaks ($\text{AuS}(\text{CH}_2)_{15}\text{CH}_3^-$, $\text{Au}_2\text{S}(\text{CH}_2)_{15}\text{CH}_3^-$, $\text{Au}[\text{S}(\text{CH}_2)_{15}\text{CH}_3]_2^-$) increase slightly, most probably due to the change of the work function. Additionally, after the water rinse, both positive and negative spectra of the $-\text{S}(\text{CH}_2)_{15}\text{CH}_3$ monolayer are almost the same as the original spectra, except for a small K^+ residue.

All these data suggest that no chemical reaction occurs. This result is in qualitative agreement with previous work [9] on the behavior of sodium atoms on a $-\text{S}(\text{CH}_2)_{21}\text{CH}_3$ SAM on Au.

After K deposition on $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$, the tail group related peaks, for example, the CO_2H^+ peak from $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ film and the CO_2CH_3^+ peak from $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ film, decrease quickly, but the K_2O^+ , K_2O_2^+ , and $(\text{CH}_2)_n\text{CO}_2\text{K}_2^+$ peaks become visible. This result suggests that both the $-\text{CO}_2\text{H}$ and $-\text{CO}_2\text{CH}_3$ groups react with K atoms, forming $-\text{CO}_2\text{K}$ adducts. Actually, after K deposition, the spectra of $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ and $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ samples are very similar, implying that a similar structure on both films forms after K deposition.

In an attempt to determine whether K atoms penetrate through the SAMs, 1.2 nm of K, equivalent to three atomic layers, was deposited on the samples. The samples were then removed from vacuum, rinsed with pure water, and returned to the analysis chamber. The K^+ peak of a $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ sample processed in this fashion is shown in Fig. 2. Only a small amount of K^+ remains in the system after the water rinse. We believe that most K atoms (both K atoms of CO_2K groups and charge-free K atoms) react with water

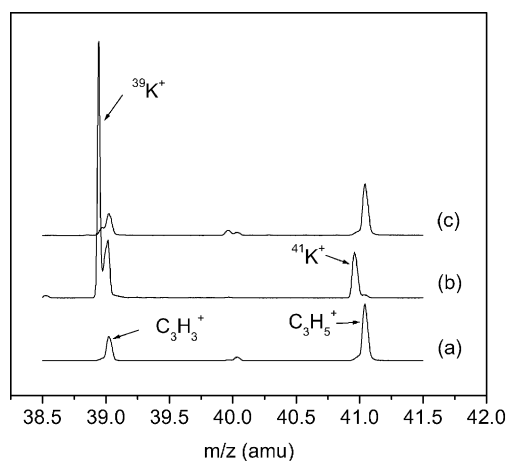


Fig. 2. Positive ion spectra of: (a) a $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ monolayer, (b) the sample after 1.2 nm K deposition, and (c) the sample after 1.2 nm K deposition and water rinse. In spectrum (b) the intensity of the $^{39}\text{K}^+$ is saturating the detector and the peak observed near 39.02 is actually due to a spurious oscillation, and not to the C_3H_3^+ ion.

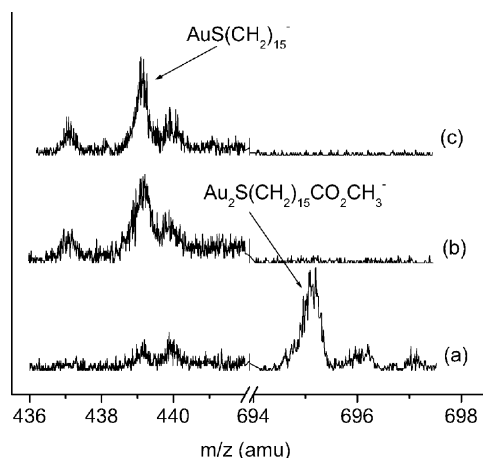


Fig. 3. Negative ion spectra of: (a) a $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ monolayer, (b) the $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ monolayer after 1.2 nm K deposition and water rinse, and (c) a $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ sample.

molecules and are then rinsed by further water. This is strong evidence that most of the K atoms stay at the vacuum interface and do not penetrate through the organic layer, because, if K atoms get to the Au–S interface, water rinsing theoretically would not remove them due to the compact structure of the film. Similar results are also found for the $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ system.

Comparing the spectra of a $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ monolayer and the same sample after 1.2 nm of K deposition and water rinse, it is found that they are almost identical, with only slightly difference in peak intensities. This result indicates that the organic molecules are not destroyed after 1.2 nm K deposition.

An interesting result is that the spectra of the $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ sample after 1.2 nm of K deposition and water rinse are almost the same as the spectra of the $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ sample. The $\text{AuS}(\text{CH}_2)_{15}^-$ peak is shown in Fig. 3. This peak is characteristic of the $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ monolayer, and the $\text{Au}_2\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3^-$ peak is characteristic of the $-\text{S}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ monolayer. This result indicates that almost all $-\text{CO}_2\text{CH}_3$ groups react with K atoms, forming $-\text{CO}_2\text{K}$ groups and the $(-\text{S}(\text{CH}_2)_{15}\text{CO}_2-)$ moiety of the $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ molecule is not destroyed during K deposition.

As the data suggest, K atoms react with the $-\text{CO}_2\text{H}$ and $-\text{CO}_2\text{CH}_3$ group, forming a $-\text{CO}_2\text{K}$ layer at the surface, but do not destroy the organic

molecules. More importantly, the $-\text{CO}_2\text{K}$ layer seems to block further K atoms from penetrating through the film, indicating a surface $-\text{CO}_2\text{K}$ layer may be a good barrier to block metal penetration. This layer may also protect organic molecules from the destruction of more chemically active metals such as Ti and Ca. Thus, with an ionic surface layer such as $-\text{CO}_2\text{K}$, SAM-based nano-electric devices might be able to be fabricated free of defects associated with metal penetration and organic molecule damage.

4. Conclusion

The ToF-SIMS approach is powerful for the study of the behavior of K atoms on organic thin films such as those examined here. The data show that the $-\text{CH}_3$ groups do not react with K atoms and that the sticking probability of K atoms on the $-\text{CH}_3$ surface is quite low. Both the $-\text{CO}_2\text{H}$ groups and $-\text{CO}_2\text{CH}_3$ groups react with K atoms, forming the $-\text{CO}_2\text{K}$ adduct. Additional K atoms stay at the vacuum interface and do not penetrate through the organic thin films. At the same time, K atoms do not destroy the backbone of organic molecules. A surface $-\text{CO}_2\text{K}$ layer may be a promising buffer layer to block metal penetration and protect monolayer molecules.

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