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Adventures in molecular electronics: how to attach wires to molecules

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Abstract

Films of both methoxy-terminated alkanethiols and a molecular wire candidate on Au{1 1 1} substrates were exposed to a variety of transition and alkali earth metals (Al, Au, Ag, Ca, Cr, Fe, Cu, Mg, Ti). The results show that aggressively reacting metals, such as Ti, destroy the organic monolayer and metals of intermediate reactivity, e.g. Cu, react at the termini and also penetrate the monolayer and react with the substrate. The results of these investigations provide a basis by which future construction of molecular devices based on desired chemical reactivity may proceed.

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1. Introduction

Molecular electronic devices may embody the next architectural advancement in computer technology; however, one of the many impediments to engineering such an electronic array is contact formation. Molecular wires [1] are intriguing molecules that show immense promise as components in electronic devices of variable functionality. Simple molecular electronic devices synthesized in silicon nanopores yield non-linear electrical response [2], but little is known about the nature of the metal/wire interaction. The chemical interactions between these device components must be known before an entire device may be constructed.

Organic self-assembled monolayers (SAMs) have proven to be a useful model for probing the potential chemistry of a device. It has been discovered that

SAMs are controllable at the molecular level by altering headgroup, tailgroup, or backbone composition and, as a result of this chemical diversity, these species can provide a densely packed array of virtually any functional group at the vacuum interface. In studying contact formation, evaporation of metal atoms upon self-assembled thin organic films is proposed to proceed by three main routes of reactivity: reaction at the vacuum interface, penetration through the organic layer and subsequent reaction with the underlying substrate, and destruction of the organic film.

Recent measurements suggest the TOF-SIMS provides direct and unambiguous information about the chemical processes that are associated with the metal contact formation [3]. For example, the appearance of MSH_2^+ cluster ions are a clear signature for penetration while metal atoms complexed with surface functional group fragments reveal bonding on top of the organic film. Here we examine the reactivity of various metal atoms with $\text{HS}-(\text{CH}_2)_{16}-\text{OCH}_3$ and a

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potential molecular wire candidate, 4-[4'-(phenylethynyl)-phenylethynyl]-benzenethiol (PEPEB) [4]. The results show that TOF-SIMS is uniquely capable of following the reaction chemistry, opening new avenues for control in synthesizing novel molecular electronic devices.

2. Experimental

The HS-(CH₂)₁₆-OCH₃ films were prepared by immersion of a Au/Cr/Si(0 0 1) wafer in millimolar solution of the thiol in absolute ethanol for several days [5]. Verification of monolayer order was performed by infrared spectroscopy and ellipsometry. Synthesis and self-assembly of the PEPEB molecular wire sample was prepared by standard published methods [4].

The experimental apparatus used to perform these experiments is based upon a previous design discussed elsewhere [6]. Modifications to this design include an additional, differentially pumped chamber to provide for metal deposition exclusively, thereby minimizing the potential for contamination and metallization of the analysis chamber. Metal deposition was conducted using a resistively heated W-wire basket and was monitored by a quartz crystal microbalance (Maxtek TM400 controller, 6 MHz Sycon crystal head) positioned approximately 45 cm from the metal source. Calibration of QCM measurements and actual deposition values was performed by AFM analysis of several metal depositions. Metals were deposited atop the samples at pressures less than 1.0×10^{-6} Torr and at a rate no greater than 1.0 Å/s. Metal coverages ranged from 0 to 10 Å including an 'infinite coverage' (usually ~100 Å). The source metals used for deposition were Al, Cu, Ti, Au, Cr, Fe, Pd, Ag, Ca, and Mg each having a purity of at least 99.5%. TOF-SIMS spectra were collected as a 15 keV Ga⁺ beam was rastered across a 100 μm² portion of the sample for two million pulses.

3. Results

Interaction at the vacuum interface of the methoxy-terminated SAMs with the metal atoms can be easily determined by the formation and growth of a metal-

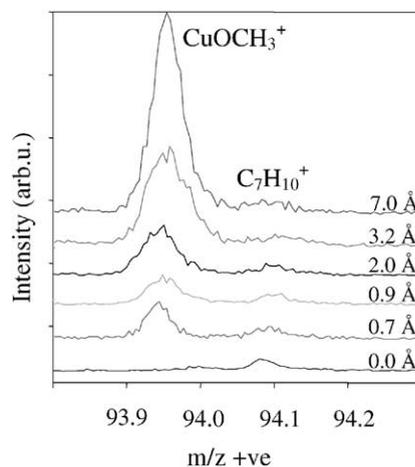


Fig. 1. +SIMS spectrum of Cu/methoxy system showing termini interaction.

OCH₃⁺ peak. As seen in Fig. 1, the ⁶³CuOCH₃⁺ peak at 93.95 amu grows in immediately as the copper is deposited and continues to populate the interface as more copper is added to the system. This mode of interaction is witnessed in the spectra of Al, Ag, and Mg with the methoxy termini evident by the presence of AlOCH₃⁺, ¹⁰⁷AgOCH₃⁺, and ²⁴MgO⁺ peaks at 58.00, 137.94, and 39.97 amu, respectively.

Evidence for penetration through the monolayer and subsequent reaction with the thiol headgroup is provided by secondary ions containing both deposited metal and thiol species. For example, M-SH₂⁺ and M-AuS⁻ both bear these species and are prominent peaks in spectra for this reaction type. In the positive ion spectra of the Cu/methoxy system shown in Fig. 2a, a CuSH₂⁺ peak at 96.99 amu increases in intensity as more copper penetrates the monolayer and reacts with the underlying substrate. Likewise, in the negative ion spectrum seen in Fig. 2b, growth of the AuCuS⁻ at 291.91 amu alludes to this phenomenon as well. This behavior was also determined to be present in the Au, Al, Cu, and Ag systems by virtue of the presence of metal/thiol moieties in their respective SIMS spectra.

Degradation of the monolayer is the third potential reaction type between the organic layer and metal species. Titanium, arguably the most reactive metal in our deposition series, virtually eliminates the monolayer at minimal deposition levels. Data in Fig. 3 shows this destruction in terms of the signal loss of the long alkyl backbone of the methoxy SAM.

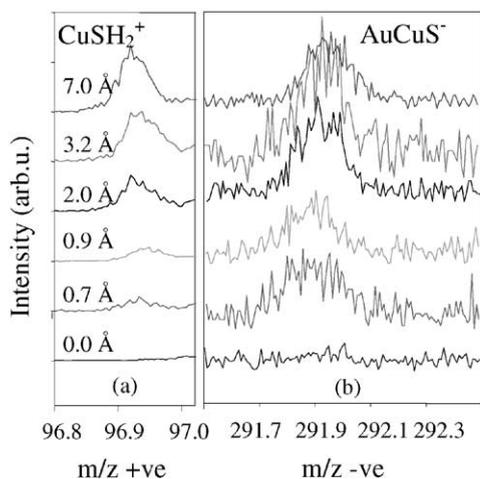


Fig. 2. +SIMS (a) and -SIMS (b) spectra of the Cu/methoxy system showing evidence of penetration of the organic layer.

Calcium was also found to have a similar deleterious effect on the organic layers.

The PEPEB samples were studied for reaction with Au, Ti, Fe, Cr, Cu, Ag, and Al. With the exception of Ti which destroyed the molecular wire array, the spectra from these depositions suffer from low signal throughout the entire mass spectrum, providing little evidence of the reactions present in the methoxy SAM systems. However, the Cu/PEPEB spectra possess several peaks indicative of a potential reaction between the metal and molecular wire. One of the

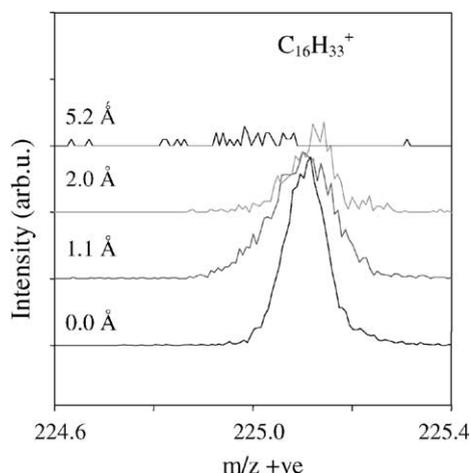


Fig. 3. +SIMS spectrum of the destruction of the SAMs alkyl backbone by Ti.

peaks, located at 139.97 amu in the positive ion spectrum is attributed to a $\text{Cu-C}_6\text{H}_5^+$ species. Data from FTIR investigations might further elucidate more details associated with the chemical reactions.

4. Discussion

The $\text{HS-(CH}_2\text{)}_{16}\text{-OCH}_3$ used in these experiments strongly chemisorb (~ 2 eV bond) in a $(\sqrt{3} \times \sqrt{3})\text{R}30$ pattern atop the polycrystalline Au (1 1 1) substrate providing a well-ordered surface for study of chemical reactivity with a multitude of metals. The results from these studies show a range of reactivity associated with the various deposited metals. The most intriguing mode of reaction is the penetration of the organic layer. Molecular dynamics simulations [7] have shown that transient defects in the monolayer can form providing the deposited metal atoms a site of insertion into the monolayer which then may promote intercalation through the monolayer to the substrate surface and subsequent reaction with it. This is a plausible explanation of the method of monolayer penetration; however it is still unclear why all the metals do not exhibit this penetration if it is merely a topographical phenomenon. Low-temperature studies are being conducted in our laboratory to determine if this route of chemistry can be slowed or even ceased by freezing the SAM molecules on the substrate and not permitting any temperature induced defect formation.

Another interesting phenomenon is observed for Au deposition on the methoxy SAMs. It is speculated that the Au completely penetrates through the monolayer. Evidence for this effect exists as a periodicity in the peak intensity for the methoxy SAM molecules and the lack of attenuation of those peaks in the “infinite” deposition sample. Finally, Pd was attempted as a deposited metal, however, the numerous isotopes present for that particular element creates much difficulty in spectral analysis. Current attempts at procuring isotopically enriched sources are underway.

The PEPEB molecule, which is known to form ordered, incommensurate SAMs shows none of the typical reactions evident in the methoxy SAM data. An explanation of the lack of the penetration seen in the alkyl SAM, can be derived based on the intermolecular interactions at play in an SAM array of

PEPEB. Contrasting the alkyl system, STM investigations show that SAMs of this molecule do not form commensurate layers and adsorb atop Au (1 1 1) sites based solely on intermolecular interactions, not substrate site specific. These interactions could allow for a greater molecular density and a steric hindrance to penetration. The impetus of adding Fe and Cr to the list of metals for the PEPEB system is directed by the potential of transition metal reaction with the π systems in the phenyl rings and the alkyne species. The ability to react at those molecular sites is limited by the opportunity of the metal atoms to penetrate the layer, and it is likely that defects are not common in this system.

5. Conclusion

Metal reactivity with methoxy-terminated SAMs at room temperature has been investigated for the following metals: Al, Cu, Ag, Au, Mg, Ca, Ti, and Pd. Reactions at the methoxy tailgroup were found to be present for Al, Ag, Mg, and Cu, while penetration through the monolayer presumably caused by temperature-induced diffusion of the methoxy SAM to form defects and allow reaction at the headgroup were witnessed in the spectra of deposited Au, Al, Cu, and Ag. Both Ti and Ca destroy the thin organic film. The molecular wire SAM was subjected to deposition of Al, Au, Ag, Fe, Cr, and Cu. The spectra shows little

evidence for reaction between PEPEB and the metals, except for Ti, which attacks and destroys the SAM, and Cu, which appears to react with a phenyl group of the molecular wire. These results illustrate the potential for molecular electronic design based on chemical reactivity and the key role that TOF-SIMS plays in chemical analysis of these systems.

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