

Thermal Decomposition of Octanethiolate Self-Assembled Monolayers on Cu(111) in UHV

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Octanethiol ($\text{CH}_3(\text{CH}_2)_7\text{SH}$) based self-assembled monolayer on Cu(111) in ultra-high vacuum has been examined using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), intergrated desorption mass spectrometry (IDMS), and contact angle analysis. The results show that the octanethiolate monolayers similar to those on gold are formed on Cu(111). The monolayers are stable up to temperatures of about 480 K. Above 495 K the monolayers decompose *via* the γ -hydrogen elimination mechanism to yield 1-octene in the gas phase. The thiolate head groups on the copper surface change to Cu_2S following the decomposition of hydrocarbon fragments in the monolayers at about 605 K.

Key Words : Self-assembled monolayers, Octanethiol, Cu(111), Thermal decomposition

Introduction

Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. They have been shown to be useful as passivating layers and also for the modification of surface properties. Potential applications include wetting, adhesion, friction, chemical sensing, ultra-fine scale lithography, protection of metals against corrosion.^{1,2} Several different varieties of SAMs have been investigated, including alkanethiols ($\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$) on Au, Ag, and Cu, and alkyltrichlorosilanes ($\text{CH}_3(\text{CH}_2)_{n-1}\text{SiCl}_3$) on SiO_2 , Al_2O_3 , and mica.¹

The majority of work on SAMs has focused on their fundamental importance in understanding interfacial properties as well as their potential application in technologies. In the case of alkanethiols on Au(111) surface, they are strongly chemisorbed on the gold surface by the formation of a covalent-like bond between gold and sulfur atoms following cleavage of a sulfur-hydrogen bond. The chemisorption of alkanethiols with long hydrocarbon chains provides densely packed SAMs on the surface. The SAMs on copper surfaces have been found to be effective inhibitors for copper corrosion.³ Because of a high blocking effect of the films, the densely packed monolayers can be applicable for protective films on copper surface against corrosion. The alkanethiolate monolayers have been prepared on copper surfaces and characterized by IR reflection, XPS, and wetting property measurements. Although the Cu surfaces differed in structural details from Au(111) surface, it has been concluded that the structures of SAMs on copper are qualitatively similar to those on gold. Laibinis and Whitesides reported that alkanethiols adsorb from solution onto copper surfaces and form densely packed SAMs.⁴ The adsorbed species is a thiolate, and the hydrocarbon chain is

primarily trans-extended and is oriented close to the surface normal.

The thermal behavior of SAMs has been studied not only to understand the chemical interaction between the head group and the substrate, but also to consider the applications. To successfully incorporate these films into the production of low surface energy structures, it is necessary for the films to withstand the temperatures used in subsequent processing and packaging steps. Alkylsiloxane monolayers on oxidized silicon have been observed to decompose beginning at about 470 °C through the cleavage of C-C bonds, resulting in a gradual decrease in chain length.⁵ Alkyl monolayers on silicon are stable up to about 340 °C and desorption of alkyl chains takes place through β -hydride elimination pathway.⁶ In a thermal desorption spectroscopy (TDS) study of octadecanethiolate SAMs on Au(111), desorption of entire chains was observed at about 177 °C, indicating that desorption takes place through cleavage of the Au-S bond.⁷ The alkanethiolate monolayers on the clean copper surfaces are stable in air up to 140 °C. Above 160 °C the monolayers begin to desorb through the oxidation reaction of the thiolate to sulfonate.⁸ However, the thermal decomposition of alkanethiols on copper surface has not been examined previously in vacuum. In this paper, we examine the thermal decomposition of octanethiolate monolayers on Cu(111) in UHV.

Experimental Section

Sample Preparation. The experiments reported here were carried out in a stainless steel ion-pumped ultrahigh vacuum chamber with a base pressure of 1×10^{-10} torr. The chamber was equipped with a x-ray photoelectron spectrometer, an ultraviolet spectrometer, a quadrupole mass spectrometer, an ion gun, a heating-cooling sample holder, and a doser. The doser is pumped by a turbomolecular pump. A Cu monocrystal which was 10 mm in diameter and 2 mm thick with

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faces oriented to the $\{111\}$ plane within $\pm 0.5^\circ$ was used in the experiments. The surface was mechanically polished using a combination of diamond and alumina paste down to a $0.05 \mu\text{m}$ size. The copper crystal was cleaned by repeated cycles of argon-ion sputtering and annealing. After each cleaning, the cleanliness of the crystal was confirmed by XPS.

Octanethiol (Aldrich, 99+% liquid purity) was introduced into the chamber through a variable leak valve (Granville-Phillips) and discharged from a nozzle located 3 cm above the substrate at room temperature. Prior to the dosage, the octanethiol was purified by a series of freeze-pump-thaw cycles using liquid nitrogen. The absolute exposures to octanethiol and absolute coverages are unknown, with relative doses given only by dose time. The XP S(2p) peak intensity increases with exposures and is saturated above 500 L. The quality of the octanethiolate monolayer was checked by water contact angle, which was 115° , in good agreement with values for alkanethiolate monolayers on Au substrates.⁴

Analysis Techniques. All XP spectra were recorded on a VG Scientific ESCALAB MK II spectrometer using Mg K α source run at 15 kV and 10 mA. Peak areas were calculated using Shirley background subtraction and were corrected by the elemental sensitivity factors.⁹ Thermal desorption experiments were performed with a differentially pumped quadrupole mass spectrometer (Balzers QMG511). Integrated desorption mass spectrometry (IDMS) was used to identify desorbing species from alcohol adsorbed Si(100) surfaces. IDMS was performed using the protocol described by Dubois.¹⁰ In this experiment, data acquisition for IDMS spectra began at 300 K and stopped at 900 K. During temperature programmed desorption (TPD) and intergrated desorption mass spectrometry (IDMS) experiments, the heating rate was 1 K/s. The copper crystal was held about 2 mm from the mass spectrometer skimmer during TPD and IDMS experiments. Contact angle analysis was performed using a model A-100 Ramé-Hart NRL goniometer to measure water contact angles in room air using the Sessile drop method.¹¹

Results and Discussion

The XP peak intensities for the octanethiolate monolayers on Cu(111) were measured as a function of annealing temperature in UHV. Figure 1 shows that the intensities of C(1s), S(2p), and Cu(2p) peaks remain almost constant at about 480 K. After annealing to 520 K, the intensity of C(1s) peak decreases, while the intensities of S(2p) and Cu(2p) peaks increases. These changes all indicate that the octanethiolate monolayers on Cu(111) are stable up to about 480 K and begin to decompose at about 500 K. Upon annealing to 600 K the monolayers have almost completely decomposed as indicated by the virtual disappearance of the C(1s) peak. However, the intensity of S(2p) peak slightly increases with increasing annealing temperature and reaches the plateau above 600 K. These observations suggest that the thiolate head groups remain on the copper surface following

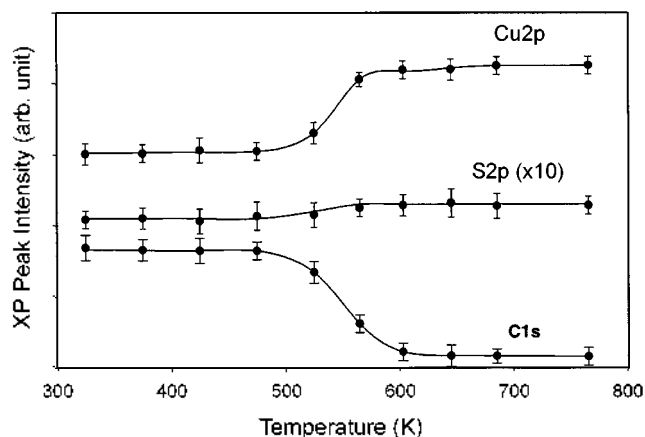


Figure 1. XP peak intensities as a function of annealing temperature for the octanethiolate monolayers.

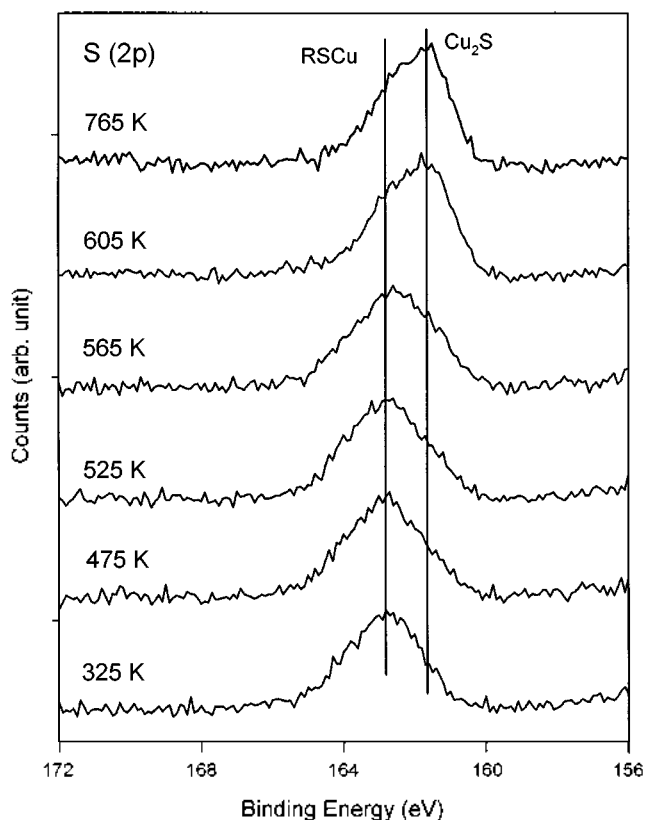


Figure 2. XP high resolution spectra of the S(2p) regions as a function of annealing temperature for the octanethiolate monolayers.

the decomposition of the alkyl chains in the octanethiolate monolayers.

High resolution spectra of the S(2p) peak for the octanethiolate monolayers on Cu(111) are shown in Figure 2 as a function of annealing temperature. The S(2p) peak initially shows up at 162.7 eV, which is assigned to the copper thiolate.⁴ As stated earlier, the S(2p) peak remains almost intact in intensity and position up to temperatures of about 475 K. The spectra show that upon annealing to 525 K, the S(2p) peak slightly increases in intensity, but remains intact

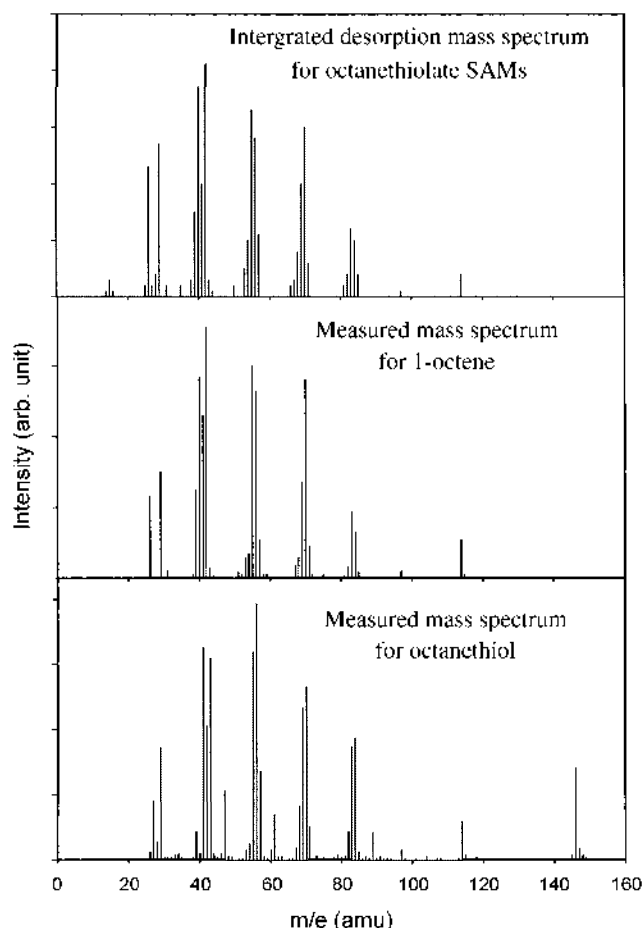


Figure 3. Integrated desorption mass spectrum for the octanethiolate monolayers.

in position. After annealing to 565 °C, the position of the S(2p) peak slightly shifts to the lower binding energy compare to thiolate. Further annealing to 605 K results in the shift of the S(2p) peak to 161.8 eV, which is assigned to Cu_2S .¹² These changes all indicate that the thiolates of the monolayers change to Cu_2S at about 605 K, which is close to the decomposition temperature of the monolayers.

The identity of desorbing species from the octanethiolate monolayers on Cu(111) was determined by the integrated desorption mass spectrum taken at 300-900 K (Figure 3). The IDMS spectrum of the desorbing species was compared to measured cracking patterns for 1-octene and octanethiol. All the peaks in the IDMS spectrum are exactly the same as the cracking fragments of 1-octene, which indicates that the desorbing species is 1-octene. Temperature-programmed desorption spectra of the octanethiolate monolayers on Cu(111) are shown in Figure 4, in which the trace are for m/e values of 114 (1-octene) and 146 (octanethiol). 1-Octene is evolved between 495 and 605 K ($T_{\text{max}} = 525$ K). The IDMS and TPD results indicate that the octanethiolate monolayers decompose above 495 K on Cu(111) via the γ -hydrogen elimination mechanism to yield 1-octene in the

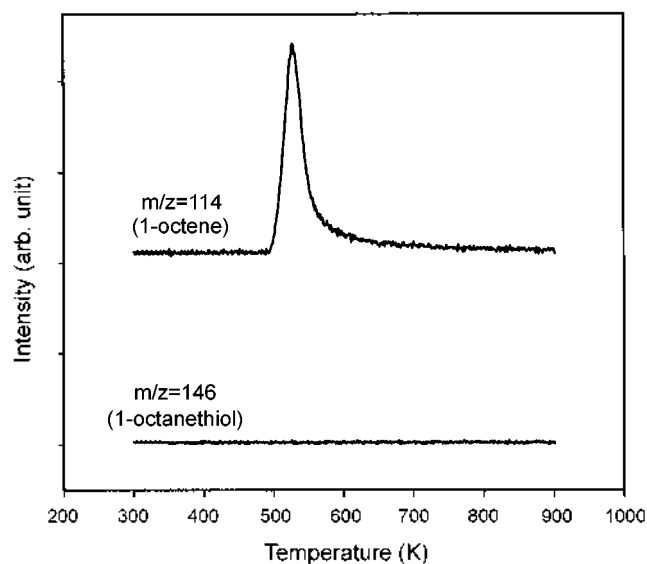


Figure 4. Temperature-programmed desorption spectra of the octanethiolate monolayers for 1-octene and octanethiol.

gas phase.

In summary, the thermal decomposition of octanethiolate SAMs on Cu(111) under UHV conditions has been studied using XPS, IDMS, TPD and contact angle analysis. The monolayers are stable up to temperatures of about 480 K. Above 495 K the monolayers decompose via the γ -hydrogen elimination mechanism to yield 1-octene in the gas phase. The thiolate head groups on the copper surface change to Cu_2S following the decomposition of hydrocarbon fragments in the monolayers at about 605 K.

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