Self-Assembled Monolayers of Alkanethiols on Clean Copper Surfaces

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Alkanethiols ($CH_3(CH_2)_{n-1}SH$) based self-assembled monolayers (SAMs) on the clean copper surfaces have been examined for n = 4, 8, and 16. Using X-ray photoelectron spectroscopy (XPS) and contact angle analysis, it is found that alkanethiolate monolayers similar to those on gold are formed on clean copper surfaces. The monolayers are stable in air up to about 140 °C. Above 160 °C the monolayers begin to desorb through the oxidation reaction of the thiolate to sulfonate, with the alkyl chains remaining intact. Following this desorption step, the copper surface has begun to oxidize to CuO at about 180 °C.

Keywords : Self-Assembled Monolayers (SAMs), Clean copper surface, Alkanethiols.

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, ultrafine scale lithography, protection of metals against corrosion.[1-3] Several different varieties of SAMs have been investigated, including alkanethiols ($CH_3(CH_2)_{n-1}SH$) on Au, Ag, and Cu, and alkyltrichlorosilanes ($CH_3(CH_2)_{n-1}SiCl_3$) 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. SAMs on copper surfaces have been found to be effective inhibitors for copper corrosion.[4] 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 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 octadecanethiol (n = 18) adsorbed 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] However, the thermal behavior of alkanethiols on copper surface has not been examined previously. In this paper, we examine the thermal stability of alkanethiolate monolayers on clean copper surfaces.

Experimental Section

Sample preparation. Polycrystalline copper sheets with thickness in the range 2 mm were used as substrates. The copper sheets were first polished with alumina powder (0.3 μm), rinsed with deionized water, and degreased ultrasonically in acetone. A chemical oxide was grown by placing the sample in a hydrogen peroxide solution at 100 °C for 15 min. The oxide layer on the copper surface was removed by etching with a 7 M HNO_3 solution for 1 min. The sample was rinsed with deionized water rapidly, followed by rinsing several times in ethanol, and then dried using nitrogen. The HNO_3 treatment has been shown to produce a metallic copper surface nearly free of carbon and oxygen.[8] The clean copper sheets were transferred under a positive flow of nitrogen to a 2.5 mM solution of the alkanethiols (hexadecanethiol (HDT), Aldrich, 99% purity; octanethiol (OTT), Aldrich, 99%; butanethiol (BTT), Aldrich, 99%) dissolved in deoxygenated ethanol for 3 hr. Monolayer deposition was carried out at room temperature. The samples were then ultrasonically washed in ethanol to remove excess reactants and dried with nitrogen. The quality of the monolayer was checked by water contact angle, which was 120° for HDT-coated Cu, 115° for OTT-coated Cu, and 105° for BTT-coated Cu.

Immediately after the samples prepared, the SAMs-coated samples were placed into a temperature and humidity chamber. We can simultaneously control relative humidity and temperature. The samples were annealed at temperatures

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between 25 and 220 °C for 10 min. Relative humidity was kept fixed at 50%.

Analysis techniques. Samples were introduced into XPS chamber by means of a load lock system. Both the XPS chamber and the load lock have been described previously.[9] The base pressure is 1×10^{-10} Torr. All XP spectra were recorded on a VG Scientific ESCALAB MK II spectrometer using Mg Kα source run at 15 kV and 10 mA. The binding energy scale was calibrated to 284.6 eV for the main C 1s peak. Each sample was analyzed at a 90° angle relative to the electron analyzer. Peak areas were calculated using Shirley background subtraction and were corrected by the elemental sensitivity factors.[10]

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

Formation of alkanethiolate monolayers on clean copper. The fully formed monolayers on the clean copper were characterized using XPS and contact angle analysis. Figure 1 shows the XP survey spectra of the clean Cu and alkanethiol-coated Cu surfaces as a function of chain length. The presence of the monolayers is indicated by a large increase
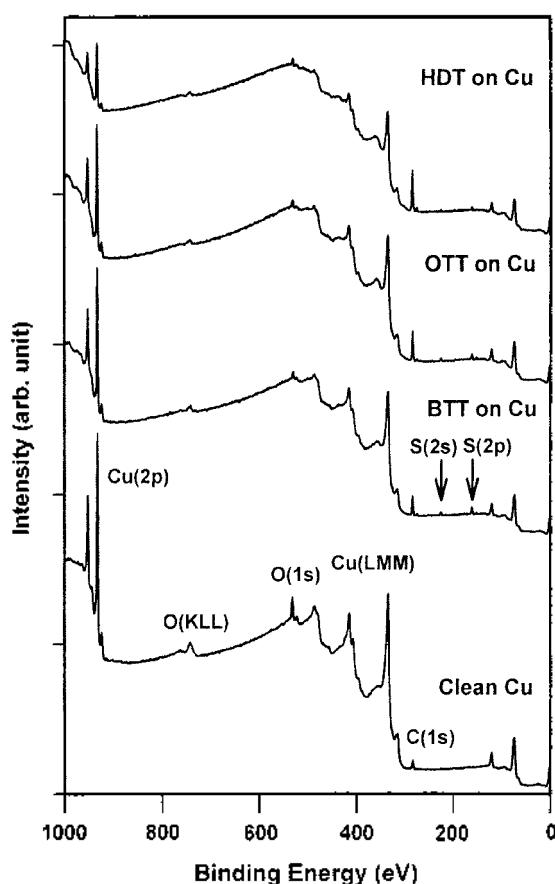
in the carbon and sulfur peak intensities, and a decrease in the copper peak intensities. The carbon peak intensity increases as the chain length increases, and is clearly due to the alkyl chains of the monolayers. The appearance of sulfur peaks is due to the Cu-S bonds which are formed between the head groups and the substrate. The sulfur peak is most intense for the shortest monolayer, and decreases in intensity as the chain length increases: smaller intensities are observed for the longer chain lengths because of photoelectron attenuation effects. The high resolution XP and Auger spectra for the clean Cu and HDT-coated Cu surfaces are shown in Figure 2. The peak positions of Cu(2p), Cu(LMM), and S(2p) peaks for various copper compounds are summarized in Table 1. The intensity of the Cu(LMM) peak at 916.5 eV (on kinetic energy scale) increases from clean Cu to HDT-coated Cu, which indicates the clean Cu(0) surface is partially oxidized to Cu(+1) by the monolayer formation. The binding energies of the S $2p_{3/2}$ and $2p_{1/2}$ peaks (162.4 and 164.9 eV, respectively) are also within the range expected for surface thiolate. With these assignments, the surface species generated from the adsorption of the alkanethiols on the clean Cu is a surface thiolate, RSCu(+1).

In the case of alkanethiols on the clean copper, the adsorption reaction is considered formally as an oxidative addition
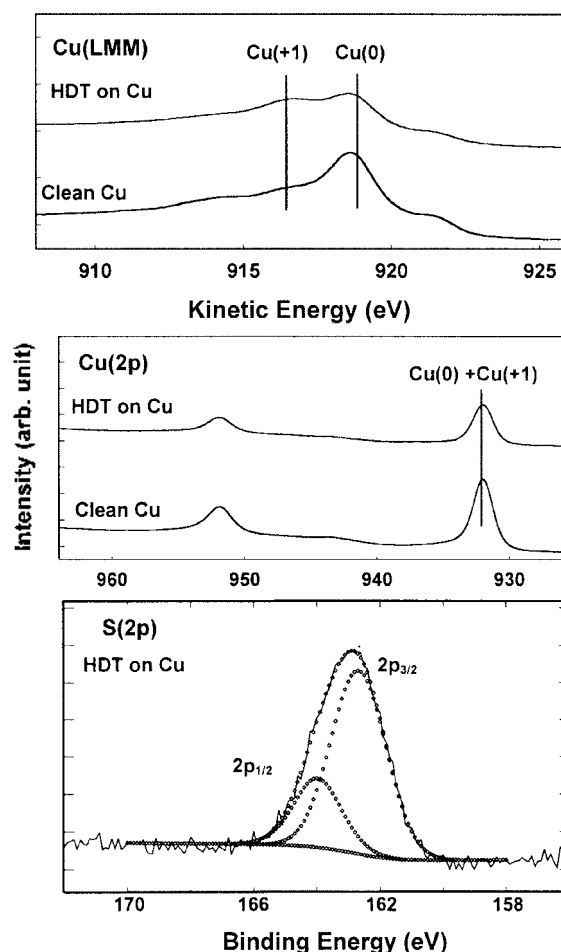

Figure 1. XP survey spectra of clean Cu, BTT-coated Cu, OTT-coated Cu, and HDT-coated Cu. In each case, the copper was etched with HNO₃ before being placed in the monolayer solution.

Figure 2. XP high resolution spectra of clean Cu and HTD-coated Cu.

Table 1. Kinetic Energies of Cu(LMM) Auger peaks and Binding Energies of Cu(2p₃₂) and S(2p) XP peaks for Various Copper-Containing and Related Compounds

compound	Kinetic energy (eV)	Binding energy (eV)		reference
	Cu(LMM)	Cu(2p₃₂)	S(2p)	
Cu	918.5	932.8		12
	918.6	932.7		12
	918.8	932.6		13
Cu₂O	916.5	932.8		12
	917.2	932.5		12
	916.5	932.5		12
CuO	917.7	933.5		12
	918.0	933.8		13
	917.8	933.6		12
Cu(OH)₂	916.5	934.6		13
	916.7	934.7		14
Cu₂S	918.0	932.6	161.8	13
	916.7	932.9	161.9	12
CuS	918.1	932.5	162.5	12
CuSO₄	915.9	935.2	168.8	12
CuSC₁₈H₃₇			162.1	4

of the S-H bond to the copper surface.[1,15] From the XPS data and the adsorption mechanism, the HDT-coated copper surface contains metallic Cu(0) and Cu(+1) of thiolate.

Thermal decomposition of alkanethiolate monolayers on clean copper. The water contact angle and XP peak intensities for a HDT-coated Cu were measured as a function of annealing temperature in air. Figure 3 shows that the contact angle remains almost constant at about 120° to 140 °C and then rapidly declines above 160 °C. The intensities of C(1s) and S(2p) peaks also remain intact up to temperatures of about 140 °C. After annealing to 160 °C, the intensities of C(1s) and S(2p) peaks decrease, while the intensity of O(1s) peak increases. Upon annealing to 180 °C the monolayer has almost completely desorbed as indicated by the virtual
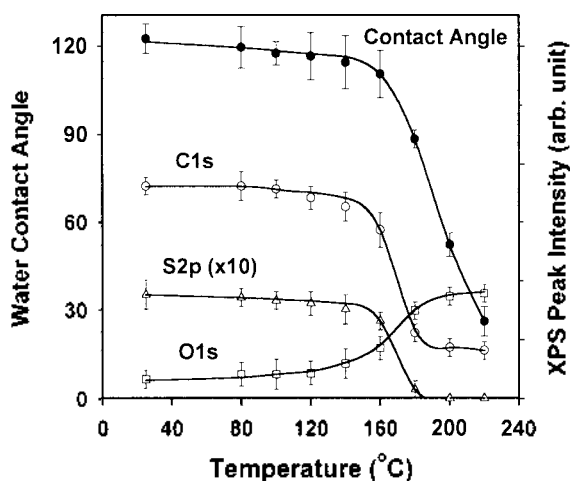
Figure 3. Water contact angle and XP peak areas as a function of annealing temperature for the HDT-coated Cu.
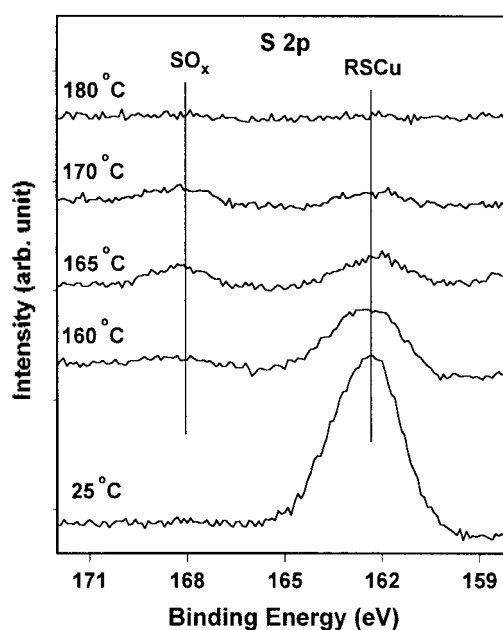
Figure 4. XP high resolution spectra of the S(2p) regions as a function of annealing temperature for the HDT-coated Cu.

disappearance of the S(2p) peak. These changes all indicate that the HDT monolayer on Cu is stable up to about 140 °C.

High resolution spectra of the S(2p) peak for the HDT-coated Cu is shown in Figure 4 as a function of annealing temperature. As stated earlier, the S(2p) peak remains almost intact in intensity and position up to temperatures of about 140 °C. The spectra show that upon annealing to 160 °C, the S(2p) peak at 162.2 eV decreases in intensity and a new peak appears at 168.4 eV. After annealing to 165 °C, the intensity of the S(2p) peak at 162.2 eV further decreases, with the peak at 168.4 eV becoming more apparent. From Table 1, the S(2p) peak at 162.2 eV is assigned to thiolate, while the peak at 168.4 eV is assigned to sulfonate. Both S(2p) peaks almost disappear upon further heating to 180 °C. These observations suggest that the HDT monolayers on the clean copper begin to desorb with the oxidation of the thiolate group at about 160 °C and completely desorb at about 180 °C.

Figures 5 and 6 show high resolution spectra of Cu(2p) and Cu(LMM) peaks for the HDT-coated Cu as a function of annealing temperature. The Cu(2p) peaks remain almost intact in intensities and shapes up to temperatures of about 160 °C. After annealing to 180 °C, the shapes of the Cu(2p) peaks change. The Cu(2p) region shows characteristic shake-up peaks and a broad Cu 2p₃₂ peak to the higher binding energy compare to Cu(+1) and Cu(0). In addition, the changes of the Cu(2p) region become more apparent with increasing the heating temperature to 200 °C. These changes all indicate that the Cu surface has begun to oxidize to Cu(+2) at about 180 °C, which is close to the desorption temperature of the monolayer. However, the spectra of the Cu(LMM) region (Figure 6) show that after annealing above 100 °C, Cu(0) species of the Cu surface slowly oxidize to Cu(+1). The Cu(+1) peak at 916.5 eV and the O(1s) peak (Figure 5) have slowly increased in intensity with increasing the
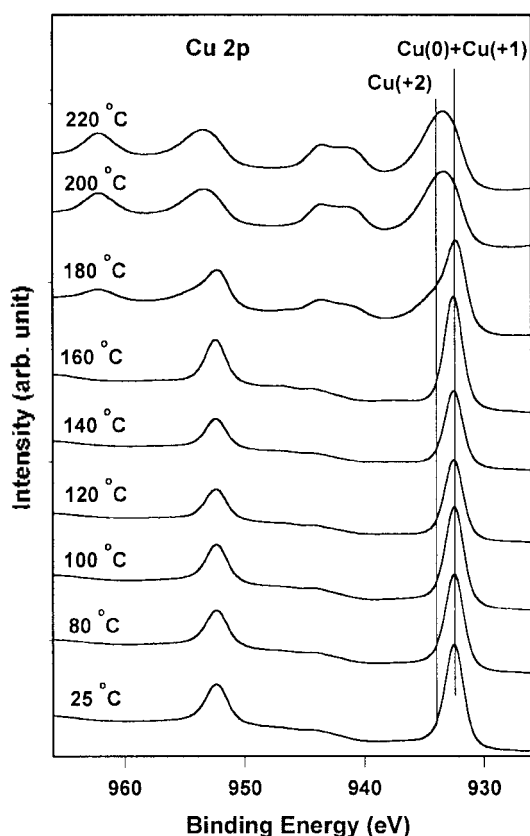
Figure 5. XP high resolution spectra of the Cu(2p) regions as a function of annealing temperature for the HDT-coated Cu.

Figure 6. Auger spectra of the Cu(LMM) regions as a function of annealing temperature for the HDT-coated Cu.

annealing temperature up to 160 °C. while the intensity of the Cu(0) peak has decreased. These changes indicate that the HDT-coated Cu surface oxidize to $Cu(+1)_2O$ before the monolayer desorbs. This initial oxidation step may be related with the oxidation of the thiolate group at about 160 °C, which will be discussed in more detail. After annealing above 180 °C, the Cu(LMM) region shows a broad single peak at 917.8 eV, which is assigned to the Cu(+2)O. As shown in the Cu(2p) region, the change of the Cu(LMM) region also indicates that the HDT-coated Cu surface following the initial oxidation step and the desorption of the monolayer has begun to oxidize to Cu(+2)O at about 180 °C.

In this paper, we have investigated the thermal stability of alkanethiolate monolayers on the clean copper surfaces under ambient conditions. XPS data indicate that the metallic copper of the HDT-coated Cu surfaces is slowly oxidized to $Cu_2(+1)O$ above 120 °C. However, the monolayers remain intact until about 140 °C. Above 160 °C the thiolates of the monolayers react with the surface oxygens (or O_2 and H_2O in air) to form sulfonates: the monolayers subsequently desorb from the copper surface. After desorption of the monolayers on the copper surfaces. the copper surfaces are oxidized to CuO or $Cu(OH)_2$ above 180 °C.

Conclusions
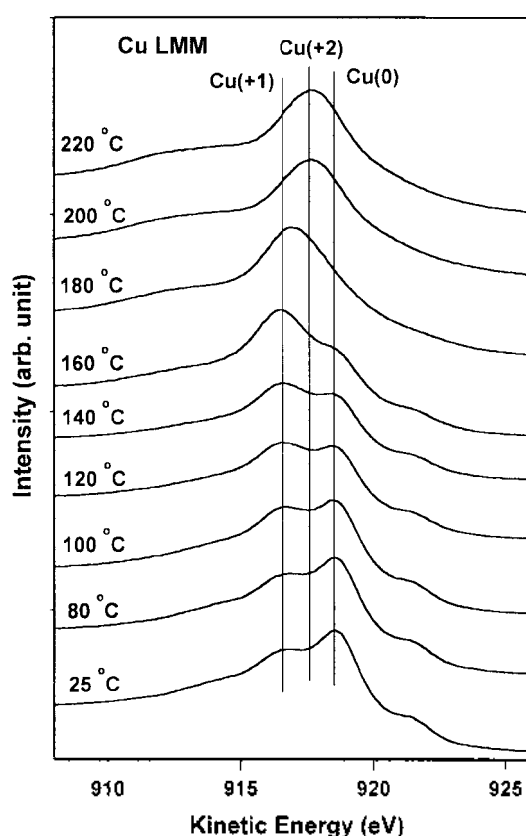
The alkanethiolate monolayers on the clean copper sur-

faces have been studied using XPS and contact angle analysis. The alkanethiolate monolayers similar to those on gold are formed on clean copper surfaces. The monolayers 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.

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