

Self-Assembled Monolayers of Alkanethiols on Oxidized Copper Surfaces

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Self-assembled monolayers of alkanethiols have been formed on oxidized surfaces of polycrystalline copper. For comparison, the monolayers were formed on clean copper surfaces. X-ray photoelectron spectroscopy (XPS), contact angle analysis, ellipsometry, and gas chromatography–mass spectrometry (GC–MS) have been employed to investigate the structure, formation, and thermal behavior of these monolayers. The results indicate that the structures of the monolayers on both surfaces are similar in quality, despite the fact that the oxidized copper surfaces were covered with the oxide layers of ~ 500 Å thickness before monolayer formation. However, the monolayers on the oxidized copper are less stable than those on the clean copper against thermal heating in air. The observation is discussed in terms of the desorption mechanism of the monolayers. XPS and GC–MS analyses for the monolayer formation on the oxidized copper surface show that thiols are actually changed to disulfides with reduction of the oxide layers.

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, and protection of metals against corrosion.^{1–3}

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 a 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 the 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 the 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. However, the SAM formation on Cu has continued to be plagued by a poor reproducibility of the alkanethiolate monolayers. It has been addressed that the differences in the formation of the monolayers on copper and gold reflect the difference in the reactivity of the surface of the copper, particularly its susceptibility to oxidation on exposure to air.^{4–6} The copper surfaces oxidize rapidly during preparation of the sample. It has been proposed

that the oxide layer on the copper surfaces may be important for reproducible formation of high-quality monolayers. In this paper, we study the effect of the oxidation of the Cu surfaces on the SAM formation.

The thermal behavior of SAMs has been studied not only to understand the chemical interaction between the headgroup 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. 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 a copper surface has not been examined previously. In this paper, we examine the thermal stability of alkanethiolate monolayers on clean and oxidized 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 oxidized copper was prepared by placing the clean copper in a hydrogen peroxide solution at 100 °C for 15 min. The thickness of the oxide layer was about 500 Å. The oxidized 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%) dis-

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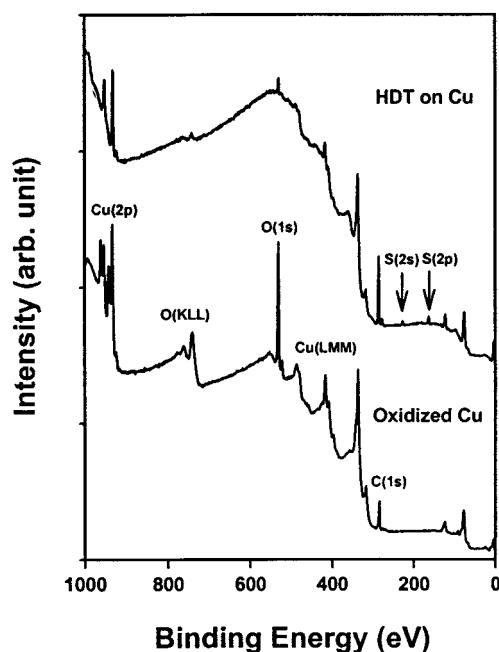


Figure 1. XP survey spectra of oxidized Cu and HDT-coated CuO. In each case, the copper was oxidized with H_2O_2 before being placed in the HDT solution.

solved in deoxygenated ethanol for 3 h. 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 CuO, 115° for OTT-coated CuO, and 105° for BTT-coated Cu, in good agreement with values for monolayers on metallic Cu surfaces.⁴ For comparison, monolayers were also formed on clean copper, using the preparation method described above. To study the formation mechanism of the monolayer on the oxidized copper surfaces, butyl disulfide was also used as a precursor.

Immediately after being prepared, the SAM-coated samples were placed in an environmental chamber, where the relative humidity and temperature were simultaneously controlled. The samples were annealed at temperatures between 25 and 220°C for 10 min. The relative humidity was kept fixed at 50%.

Analysis Techniques. Samples were introduced into the 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 was 1×10^{-10} Torr. All XP spectra were recorded on a VG Scientific ESCALAB MK II spectrometer using a Mg $K\alpha$ 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 Ellipsometry measurement was carried out using a Gaertner L116-B ellipsometer, using the optical constants of 0.24 (n) and 3.40 (k) for the Cu substrate. Because of uncertainties in the optical constants of CuO, the thickness measured for the oxide layer has an uncertainty of approximately 25%.

The BTT solutions were characterized by a model 5890 Hewlett-Packard gas chromatograph connected with a model 5971 Hewlett-Packard mass spectrometer.

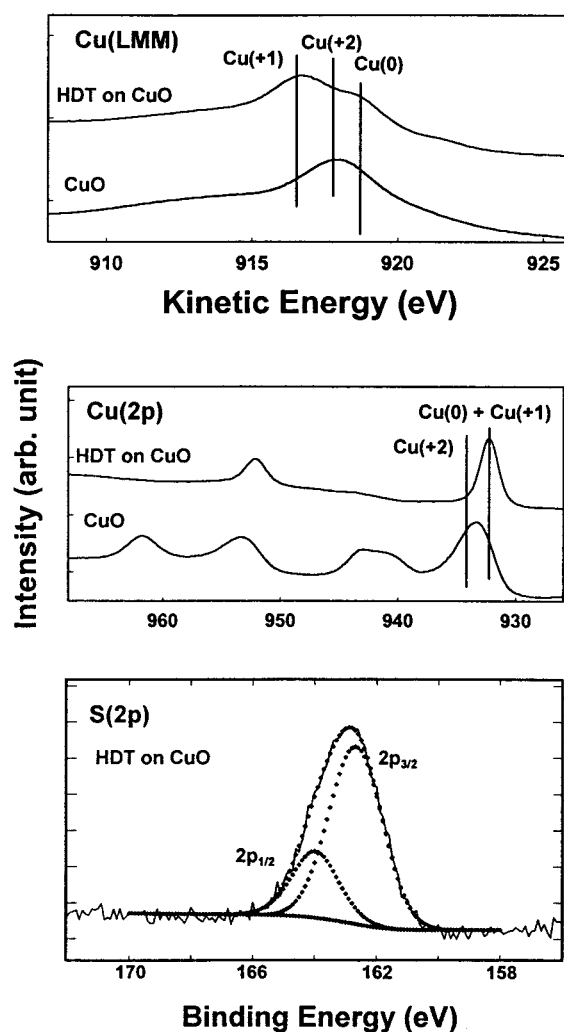


Figure 2. XP high-resolution spectra of oxidized Cu and HDT-coated CuO.

Results and Discussion

Structure and Formation of Alkanethiol Monolayers on CuO. XP and Auger spectra for the clean copper following H_2O_2 treatment are shown in Figures 1 and 2. The large O(1s) peak is observed at 530 eV, indicative of the formation of an oxide layer on the clean copper. The Cu(2p) region shows characteristic shake-up peaks and a broad Cu(2p_{3/2}) peak to the higher binding energy compared to Cu^{1+} and Cu^0 . From the XPS results, a CuO layer was grown by H_2O_2 treatment, and the thickness of the CuO layer was about 500 Å as measured by ellipsometry. The XP spectrum for the CuO layer following HDT monolayer formation, shown in Figure 1, indicates a large decrease in oxygen peak intensity. The high-resolution spectra of the Cu(2p) region show that the binding energy for Cu(2p_{3/2}) shifts to lower energy and the characteristic shake-up peaks for Cu^{2+} at ~942 eV completely disappear, after HDT adsorption on the oxidized copper surfaces (Figure 2). The peak positions of Cu(2p), Cu(LMM), and S(2p) peaks for various copper compounds are summarized in Table 1. Since the formation of the HDT monolayer on the Cu^{2+}O layer resulted in a large decrease of the oxygen peak intensity and a complete loss of peaks due to Cu^{2+}O , the adsorption of alkanethiol on the CuO surfaces must have completely removed the CuO layer. As shown in Figure 2, the S(2p) peaks are the same as those of the HDT-coated Cu, indicating that the surface species generated from the adsorption of the alkanethiols on the oxidized Cu is

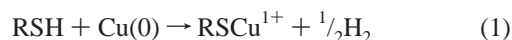
TABLE 1: Kinetic Energies of Cu(LMM) Auger Peaks and Binding Energies of Cu(2p_{3/2}) and S(2p) XP Peaks for Various Copper-Containing and Related Compounds

compd	kinetic energy (eV) Cu(LMM)	binding energy (eV)		ref
		Cu(2p _{3/2})	S(2p)	
Cu	918.5	932.8		12
	918.6	932.7		12
	918.8	932.6		13
Cu ₂ O	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
Cu ₂ S	918.0	932.6	161.8	13
	916.7	932.9	161.9	12
CuS	918.1	932.5	162.5	12
CuSO ₄	915.9	935.2	168.8	12
CuSC ₁₈ H ₃₇			162.1	4

also a surface thiolate, RSCu¹⁺. For the HDT-coated CuO, the surface species, carbon peak intensity, and water contact angle are the same as those of the HDT-coated Cu. These observations suggest that the structures of the HDT monolayers formed on the clean and oxidized copper surfaces are similar in quality. However, the HDT-coated CuO surfaces have higher oxygen content and Cu¹⁺ state than the HDT-coated Cu surfaces, which indicates that the former surfaces have not only a surface thiolate, RSCu¹⁺, but also a cuprous oxide, Cu¹⁺₂O, even after monolayer formation.

To understand the formation mechanism of the alkanethiolate monolayers on the oxidized copper surface, we analyzed a 2.5 mM solution of BTT dissolved in ethanol and the remaining solution after the monolayer formation by using GC-MS. The GC-MS data show a large increase of the mass signal of 514 [(SC₄H₉)₂] in the remaining BTT solution after the monolayer formation, which suggests that a great amount of the thiols is changed to disulfides on the CuO surfaces. This surface reaction from thiol to disulfide may reduce the Cu²⁺O species to Cu¹⁺₂O or Cu. On this reduced surface, the alkanethiolate monolayers are formed. The XPS data already showed that the CuO layers have been completely removed after the monolayer formation on the CuO surfaces. This surface reaction is confirmed by the fact that we could not make the monolayer on the CuO surfaces from (SC₄H₉)₂ solution because the disulfide could not reduce the oxide layer. The alkanethiols as well as the disulfides make indistinguishable monolayers on the clean copper.

In the case of alkanethiols on the clean copper, the adsorption reaction is considered formally as an oxidative addition of the S-H bond to the copper surface, followed by a reductive elimination of the hydrogen,¹ as usually written:



In the case of oxidized copper, the alkanethiols are not adsorbed directly on the Cu²⁺O surface, but reduce the oxide layer with disulfide formation by the following reaction:



or



This reaction continues to reduce all the CuO layer, and the

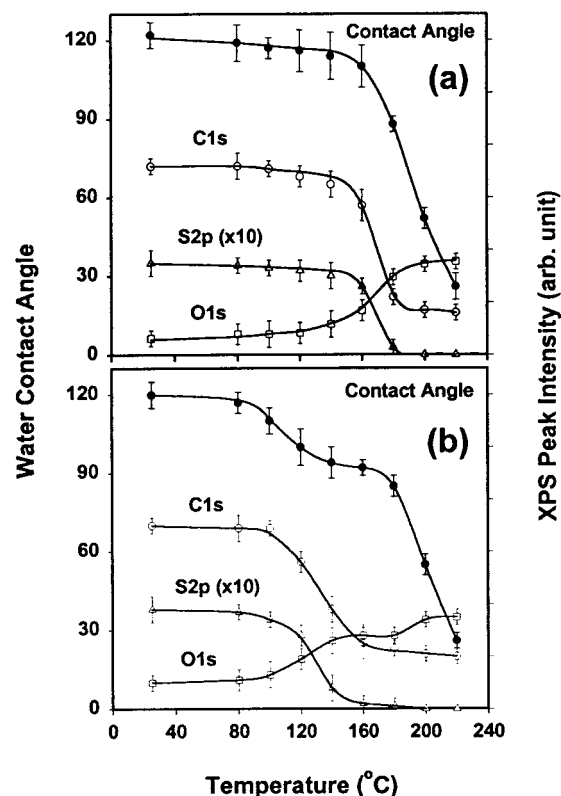


Figure 3. Water contact angle and XP peak areas as a function of annealing temperature (a) for the HDT-coated Cu and (b) for the HDT-coated CuO.

monolayer is formed on the reduced surface, by the following reaction:



or



This is confirmed by the XPS and GC-MS data which reveal no Cu²⁺ state on the oxidized copper surface and show a large increase of disulfide in the thiol solution after the monolayer formation. Such a mechanism was already discussed by two groups for alkanethiol reaction with CuO.^{15,16} Keller and co-workers also proposed that alkanethiol formed multilayers on the copper oxide powder. However, our XPS data obviously show that only a monolayer is formed on the oxidized copper surfaces because the monolayers on the oxidized copper have almost the same carbon and sulfur intensities as on the clean copper.

Thermal Behavior. The water contact angle and XP peak intensities for a HDT-coated Cu and a HDT-coated CuO were measured as a function of annealing temperature in air. Figure 3a shows that the contact angle of the HDT-coated Cu remains almost constant at about 120–140 °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 the C(1s) and S(2p) peaks decrease, while the intensity of the O(1s) peak increases. Upon annealing to 180 °C, the monolayer has almost completely desorbed as indicated by the virtual disappearance of the S(2p) peak. These changes all indicate that the HDT monolayer on Cu is stable up to about 140 °C. Figure 3b shows that the HDT monolayer on CuO begins to desorb at about 120 °C and has

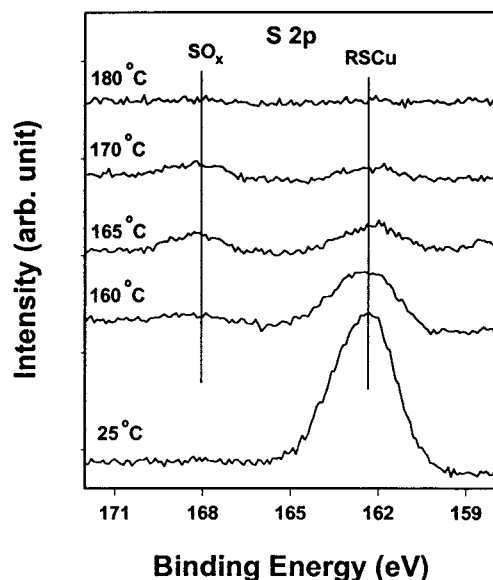


Figure 4. XP high-resolution spectra of the S(2p) regions as a function of annealing temperature for the HDT-coated Cu.

completely desorbed by 160 °C. The desorption temperature is about 40 °C lower than that found for the HDT monolayer on Cu.

High-resolution spectra of the S(2p) peak for the HDT-coated Cu is shown in Figure 4 as a function of annealing temperature. 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. The thiolates of the HDT monolayers on CuO also desorb with the oxidation at about 120 °C.

Figure 5 shows high-resolution spectra of Cu(LMM) peaks for the HDT-coated Cu as a function of annealing temperature. The Cu(LMM) peaks remain almost intact in intensities and shapes up to temperatures of about 100 °C. After annealing above 120 °C, the Cu¹⁺ peak at 916.5 eV and the O(1s) peak (Figure 3) have slowly increased in intensity with increasing the 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 oxidizes to Cu¹⁺₂O before the monolayer desorbs. This initial oxidation step may be related with the oxidation of the thiolate group at about 160 °C. Above 160 °C the thiolates of the monolayers react with the surface oxygens (or O₂ and H₂O in air) to form sulfonates; the monolayers subsequently desorb from the copper surface. After annealing above 180 °C, the Cu(LMM) region shows a broad single peak at 917.8 eV, which is assigned to Cu²⁺O. The change of the Cu(LMM) region indicates that the HDT-coated Cu surface following the initial oxidation step and the desorption of the monolayer has begun to oxidize to Cu²⁺O at about 180 °C.

Before annealing, the intensities of the Cu¹⁺ peak at 916.5 eV and the O(1s) peak on the HDT-coated CuO are much higher than on the HDT-coated Cu, suggesting that the surface has already oxidized to Cu¹⁺₂O. This surface oxide may be related to the thermal stability of the monolayer, which will be discussed in more detail. As shown in Figure 6, the Cu(LMM) peaks on

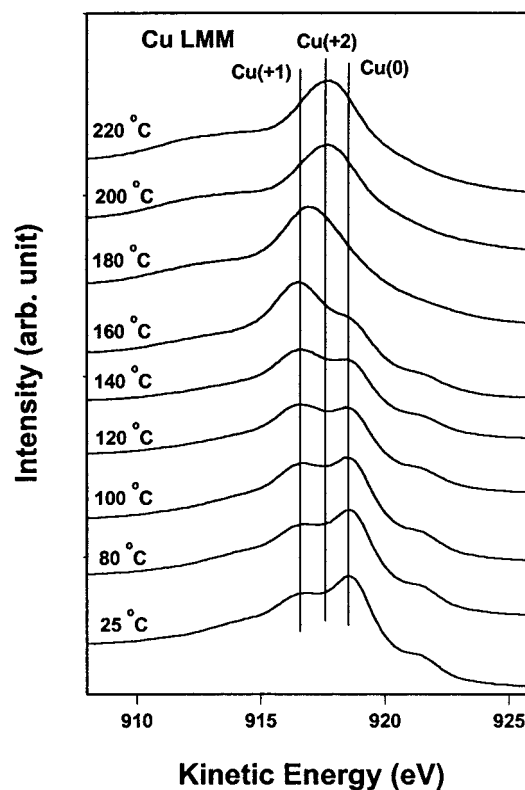


Figure 5. Auger spectra of the Cu(LMM) regions as a function of annealing temperature for the HDT-coated Cu.

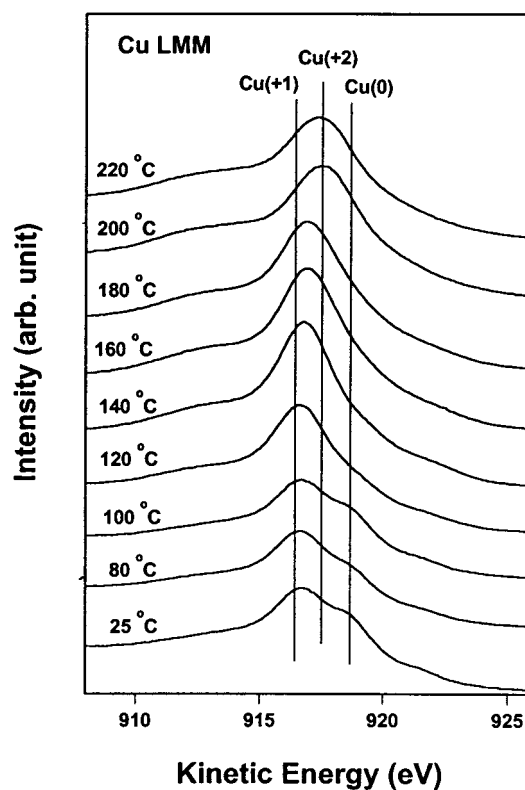


Figure 6. Auger spectra of the Cu(LMM) regions as a function of annealing temperature for the HDT-coated CuO.

the HDT-coated CuO remain almost intact in intensities and shapes up to temperatures of about 100 °C. The Cu(LMM) spectra show that upon annealing to 140 °C, the intensity of the Cu¹⁺ peak has increased, while the intensity of the Cu(0) has decreased. After annealing above 160 °C, the Cu(LMM)

region shows a broad single peak at 917.8 eV, which is assigned to Cu^{2+}O . As shown in the Cu(2p) region, the change of the Cu(LMM) region also indicates that the Cu surface has begun to oxidize to Cu^{2+}O at about 160 °C.

The monolayers on the oxidized copper surfaces have a structure similar to that of the monolayers on the clean copper surfaces, except that the former surfaces have more oxygen and Cu^{1+} contents than the latter. This difference may result in a decrease in desorption temperature. The monolayers on the oxidized copper begin to desorb at 40 °C lower temperature than those on the clean copper. One possible reason is a higher oxygen content of the monolayer-coated CuO surfaces. The desorption of the monolayers is initiated by the sulfonation reaction of the thiolate groups with surface oxygen or O_2 and H_2O in air. Due to the high content of the surface oxygen, the monolayers on the oxidized copper might be easily desorbed as alkyl sulfonate. It is also possible that the bond strength of $\text{RS}-\text{Cu}$ on the oxidized copper is weaker than that on the clean copper. The stability of thiolate groups on copper is related to the electron density on the thiolate sulfur: the more electron density on the thiolate sulfur, the weaker the bond strength of the $\text{RS}-\text{Cu}$. Since the electron density of the thiolate sulfur on the cuprous surface is probably greater than that on the metallic copper surface, the monolayers on the oxidized copper are less stable than those on the metallic copper.

Conclusions

The structure, formation, and thermal behavior of the alkanethiolate monolayers on the oxidized copper surfaces have been studied using XPS, contact angle analysis, ellipsometry, and GC-MS. The structures of the monolayers on the oxidized and clean copper surfaces are similar in quality, despite the fact that the former surfaces are covered with the oxide layers of ~ 500 Å thickness before monolayer formation. The alkanethiols

are not adsorbed directly on the oxidized copper surface, but reduce the oxide layer with disulfide formation. This reaction continues to reduce all the CuO layer, and the monolayer is formed on the reduced surface. The monolayers on the copper surfaces desorb through the oxidation reaction of the thiolate to sulfonate. The monolayers on the oxidized copper begin to desorb at 40 °C lower temperature than those on the clean copper in air.

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