Tarnish Protection of Silver Using a Hexadecanethiol Self-Assembled Monolayer and Descriptions of Accelerated Tarnish Tests

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ABSTRACT

A four-step procedure was developed for depositing a hexadecanethiol self-assembled monolayer (SAM) onto the surface of silver in order to provide tarnish resistance. The four steps may be characterized as cleaning, etching, monolayer self-assembly, and rinsing. A key observation in this work is that an optimal deposition time exists for a given concentration of the hexadecanethiol. For example, a 2 vol% solution (2 mL hexadecanethiol in 98 mL trichloroethylene) required 30 min to 60 min for optimum coating formation. The quality of the coatings was characterized using water drop contact angle measurements and electrochemical impedance spectroscopy (EIS). In addition, two tarnish tests were developed specifically for this project. One test was a lab bench vapor test that could tarnish silver, copper, or brass to a dark color within a few hours. A second test exposed the silver to a stream of a sulfide-containing foam and could tarnish silver to black within several minutes. The degree of tarnishing from these two tests was quantified by measuring the percent reflectance of the surface using visible light.

KEY WORDS: coatings, electrochemical impedance spectroscopy, hexadecanethiol, self-assembled monolayer, silver, tarnish

INTRODUCTION

Silver exposed to the atmosphere will tarnish. Hundreds of silver alloys have been created to produce a nontarnishing silver, but to no avail.[1] The black or brown tarnish layer that slowly forms on silver during exposure to the atmosphere is a silver sulfide (Ag_2S) and results from the reaction of silver with atmospheric hydrogen sulfide (H_2S) and water vapor. This Ag_2S layer continually thickens, first dulling the brilliance of the polished silver and then turning it yellow brown, and finally black as the Ag_2S layer thickens. A barrier layer is needed on the surface of silver to prevent the absorption of the H_2S and the subsequent Ag_2S reaction.

Many surface treatments have been developed to slow the tarnishing of silver. Chromates have been found to be successful, but chromates are carcinogens and are being replaced. Organic coatings have been used to slow the tarnishing reaction,[2] but they can be difficult to apply. Furthermore, a thick organic coating gives the silver a yellow appearance and reduces its luster, making sterling silver appear more like polished stainless steel. A recent development, however, is the use of self-assembled monolayers (SAM) of organomercaptans (thiols) to passivate metal surfaces such as gold,[3-8] copper,[8-11] and silver.[8,12] These SAM films are composed of long hydrocarbon molecules that attach to the surface through the sulfur atom and stand "on-end" with the hydrocarbon tail oriented to the air or solution (Figure 1). These SAM also have been used to passivate semiconductor surfaces.[13-14] Previous work that applied

SAM to silver surfaces for slowing atmospheric tarnishing used freshly deposited silver films or specially cleaned films.[8] The current work describes a procedure for using this technology to coat silver coins or jewelry without affecting the original luster or the flexibility of silver chains.

Recent developments have shown how to prepare SAM films on many surfaces using a variety of chemical compounds.[15-16] These ultrathin films are typically only a few nanometers in thickness. The current work uses alkanethiols or alkylmercaptans (a straight chain hydrocarbon with a sulfur at one end) for the film composition. When a metal is placed in the presence of thiols, the sulfur end bonds to the metal and the hydrocarbon tails align and form a compact structure oriented away from the metal, which optimizes the intermolecular van der Waals interactions. This alignment affects many of the surface properties of the sample but is undetectable to the naked eye since the layer is only 2 nm thick (Figure 1). For these reasons, SAM are an ideal way to protect a metal surface without changing its appearance.

Several works have addressed the corrosion protection offered by SAM, and several patents that describe SAM coatings on gold or silver are available.[17] Kartlücke, et al., describe coating silver with a hexadecanethiol solution or hexadecanethiol vapor.[18] Their solution was 0.2 wt% to 0.4 wt% hexadecanethiol for 3 min to 5 min or hexadecanethiol vapor (80°C for 1 h). They found that the best thiol was hexadecanethiol with 16 carbons (C16). In addition, they reported that the thiol layers possessed a self-healing ability because the alkanethiol molecules tend to creep across the surface. However, Zamborini and Crooks reported in 1997, "We conclude that while n-alkanethiol SAMs reduce the rate of corrosion, they are generally too fragile and contain too many defects to be useful for technological applications in highly corrosive environments."[19] Additional work in this area is likely to combine self-assembly with polymerization methods to create robust and compact films for corrosion inhibition.

The present paper offers new developments along several fronts. In particular, it outlines a procedure for minimizing the defects in the thiol coating so that it better withstands corrosive environments, and it demonstrates a methodology for defining the optimal parameters for the procedure. Also, two procedures are presented for corroding silver materials that allow the protective properties of the film to be quantified in a rapid but realistic manner.

EXPERIMENTAL PROCEDURES

Thiol Coating Procedure

The SAM layer was formed on the 99.9% pure silver surface using a four-step procedure:
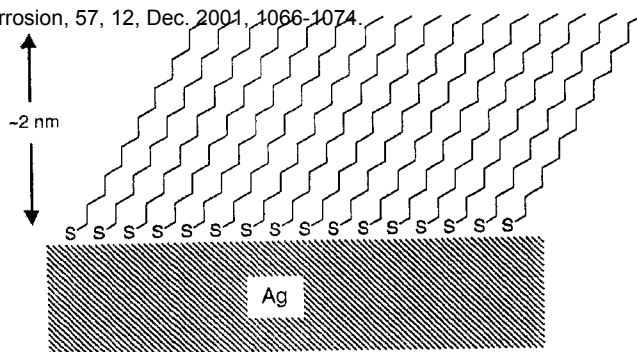
FIGURE 1. *The alkanethiols bond to a silver surface in a regular array known as a SAM. The alkanethiol drawn in the diagram is hexadecanethiol (C16 thiol).*

Step 1: Initial Cleaning — The silver was degreased with a three-stage solvent bath (trichloroethylene-acetone-ethanol) or washed in a hot alkaline bath and rinsed in distilled (DI) water to remove any dirt and oil on the sample. This step is not necessary for the coating of freshly electroplated silver.

Step 2: Acid Etch — The silver was immersed in 10% sulfuric acid (H_2SO_4) for 5 min to "activate" the silver surface, then rinsed with DI water for several seconds. The naked eye could not discern any difference between the etched and unetched surfaces. Although a coating can be applied without this acid etch step, the effectiveness of the SAM to resist tarnishing is demonstrated in this work to be greatly improved by the acid etch. DI water was used to rinse any excess H_2SO_4 from the sample and avoid contamination of the thiol solution. Other acids, including nitric acid (HNO_3), hydrochloric acid (HCl), lactic acid ($CH_3CH[OH]CO_2H$), acetic acid (CH_3CO_2H), and piranha solution (H_2SO_4 and hydrogen peroxide [H_2O_2]) were tested, but they either discolored the silver, or were not as effective as the simple H_2SO_4 etch.

Step 3: Alkanethiol Deposition — The etched silver was immediately transferred into a hexadecanethiol (or other alkanethiol) solution, and the SAM was allowed to form. An optimum deposition time was identified for a given thiol concentration.

Step 4: Final Rinse and Dry — The sample was rinsed with trichloroethylene, then spray-rinsed with DI water, and finally placed in warm circulating air to dry. If a dilute (<2%) thiol solution was used, then one may skip the trichloroethylene rinse and proceed directly to the DI water rinse. The contaminated DI water should be reacted with bleach (5% NaOCl) before disposal.

Water Drop Contact Angle

The contact angle formed between the silver sample and a water droplet provides a simple test to determine if a SAM is present on the silver surface and provides a simple measure of its quality.[15,20] Figure 2 illustrates the contact angle measurement.

Water drop

Bare silver

Ag

(a)

Water drop

Thiol-coated

Ag

(b)
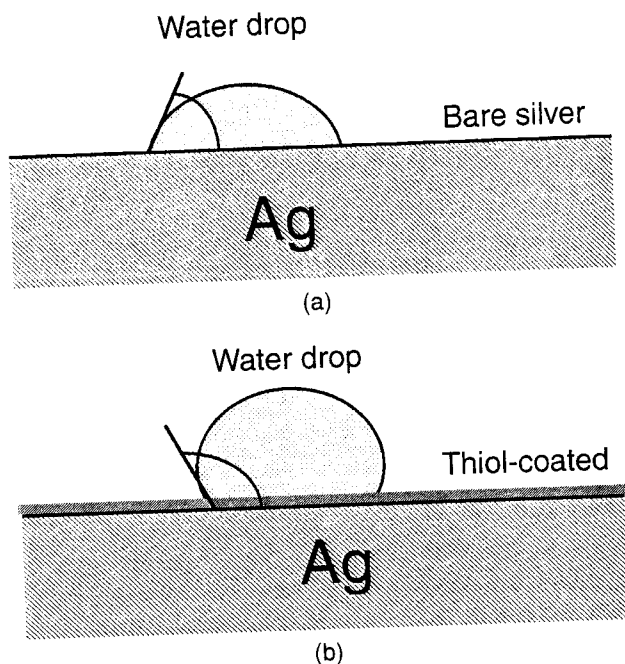
FIGURE 2. *The water drop contact angle measurement: (a) the case of a water drop that wets the bare silver surface, and (b) the case of a water drop that "beads up" on the thiol-coated surface.*

In Figure 2(a), the water droplet interacts with a bare, hydrophilic silver surface. The water droplet minimized its surface free energy by spreading (i.e., wetting the substrate), and the angle between the tangent to the water drop's surface and the substrate normal is <90 degrees. For the bare silver surface, the contact angle was found to be 61 ± 3 degrees. In contrast, the silver samples coated with an alkanethiol SAM are hydrophobic. In this situation, the water droplet minimized its surface free energy by "beading up" on the coated surface. For good quality SAM films on silver, the water drop contact angles were found to be 115 ± 3 degrees. Although the contact angle measurement provided a quick and reliable test for assessing the presence of a SAM and, to some degree, its compactness, the measured contact angle did not correlate with increased tarnish protection. Additional techniques were developed to evaluate the coated sample's resistance to tarnishing.

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was used to characterize the SAM films. In the EIS method, a small sine wave voltage (±5 mV rms) was applied to a coated sample while it was immersed in

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[1] As a note of caution, the Na₂S should never be added to neutral or acidic water because large quantities of H₂S gas can be given off, which is poisonous at 10 ppm. The human nose can detect 1 ppm of H₂S but becomes dull with exposure, so a person working in the lab should never try to tolerate an obnoxious odor. For disposal of the solution, it was mixed slowly with 60 mL of 5% NaOCl (household bleach), reacted for several hours, and then diluted and discarded.[23]
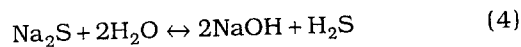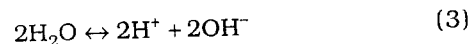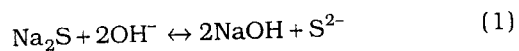
an electrochemical cell containing a 3.5% sodium chloride (NaCl) electrolyte solution. The counter and reference electrode were one and the same, polished silver. The alternating current (AC) impedance, Z, of the system was measured to obtain the AC resistance or magnitude of the impedance, $|Z|$, and the phase shift or maximum lag between the maximum current and maximum voltage. These two parameters, the phase shift and the impedance, were used to estimate the film quality and thickness. The low frequency impedance (near 0.1 Hz) revealed the presence of pinholes in the SAM by a flattening of the impedance or a decrease in the phase angle. The larger the impedance and the phase shift, the fewer the defects on the SAM. The thickness of the SAM coating can also be estimated from the capacitance by approximating the organic film as a parallel plate capacitor.[21]

Accelerated Tarnish Tests

Two accelerated tarnish tests were developed for this study. In the vapor tarnish test (Figure 3[a]), silver samples were placed above a warm solution of sodium sulfide (Na₂S) in a sealed chamber. This vapor test could tarnish silver to ~30% of its original reflectivity in 1 h. In the foam tarnish test (Figure 3[b]), a surfactant foam containing the sulfide was streamed onto the silver surface. The foam test was able to more rapidly tarnish the silver samples, reducing the silver reflectivity to 20% in 5 min. These tarnishing procedures are also useful for tarnishing copper, copper alloys, and other materials.

The corrosive vapors of the vapor tarnish test were generated from a solution containing 0.5 M sodium hydroxide (NaOH) and 0.1 M Na₂S at a temperature of 40°C to 45°C. Rankin, et al., have used a similar test, although their test used alternate immersion rather than exposure to vapor.[22] A 100-mL volume of the tarnish solution was prepared by mixing 2.5 mL of 50% NaOH with ~97 mL of DI water, and then adding 2.4 g Na₂S·9H₂O. Upon heating to 40°C to 45°C, the solution gave off a sulfur odor, presumably H₂S.[1]

The chemical equilibria in the solution were believed to be those shown in Equations (1) through (4):

$$Na_2S + 2OH^- \leftrightarrow 2NaOH + S^{2-} \tag{1}$$

$$S^{2-} + 2H^+ \leftrightarrow H_2S \tag{2}$$

$$2H_2O \leftrightarrow 2H^+ + 2OH^- \tag{3}$$

$$Na_2S + 2H_2O \leftrightarrow 2NaOH + H_2S \tag{4}$$

The tarnish solution stored well at room temperature, but it decayed in effectiveness over time and when heated. It was therefore prepared freshly for

each test. For the vapor test, the tarnish solution was placed in an enclosed chamber and the silver samples that were to be corroded were placed in the air space above the liquid (Figure 3[a]). The chamber was obtained from Bel-Art[†] (Product Catalog no. F42010-000); it had a white polypropylene base and a clear polycarbonate dome. The vapors were mixed in the chamber by a fan. The mixing fan was a Radio Shack 12 VDC[†] brushless fan, Catalog no. 273-240. The fan was bolted to the support plate in the chamber, and the holes in the support plate were enlarged to 5 mm in diameter to increase vapor circulation. The fans tended to corrode in this humid atmosphere, so after each test the fans were run for several hours in lab air until dry.

The second accelerated tarnish test passed a foaming solution of 10 mM Na_2S over the metal sample (Figure 3[b]). The foam test was prepared by placing a surfactant (a few drops of Ivory[†] dish washing soap) in the sulfide solution and then bubbling with a carrier gas. The resulting foam was piped to the metal surface (Figure 3[b]). This procedure can tarnish silver to a brown color, ~20% of its original luster, in 5 min.[2]

Reflectivity Measurement

The extent of silver tarnish was quantified by measuring the silver sample's reflectivity with a fiber optic spectrometer. The silver reflectivity (or brilliance) decreased as the sample tarnished, and the sample's corrosion could thus be quantified. An Ocean Optics S2000[†] fiber optic spectrometer was used to measure the reflectivity of the silver samples. The integrating sphere illuminated the silver sample and measured the amount of reflected light. Polished, untarnished silver was assigned the value of 100% reflectance. With this system, it was simple to measure the entire spectral response of the reflectivity; however, the values of the reflectivity at 500 nm incident light are reported here—unless otherwise specified. A silver surface with 80% reflectance was a dull color while 20% reflectance was brown.

RESULTS AND DISCUSSION

Tarnishing of Bare Silver

The two accelerated tarnish tests, although different in operation and corrosion rate, yielded qualitatively similar results. Figure 4(a) compares the corrosion rate of each test, using reflectivity of the silver sample as a measure of the corrosion. The vapor method tarnished the samples many times more

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[†] Trade name.
[2] Unfortunately, only anecdotal evidence correlates the short-term results to the long-term atmospheric tarnishing. Additional studies are needed, but any correlation will be valid only in the geographical region where it is conducted since air quality varies substantially with both seasons and regions in regard to the parts-per-billion of sulfur compounds.
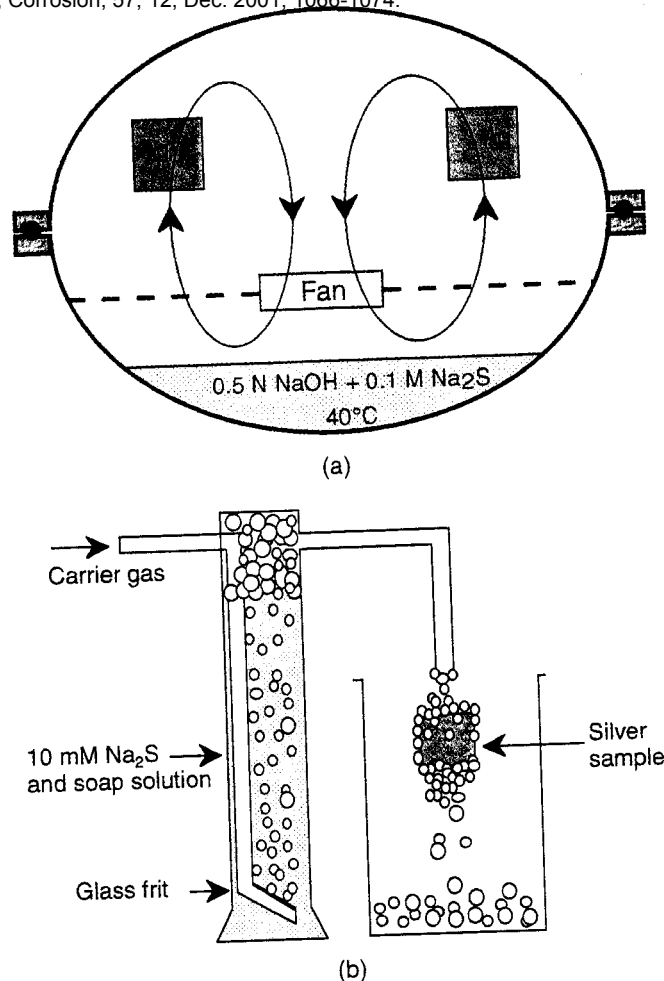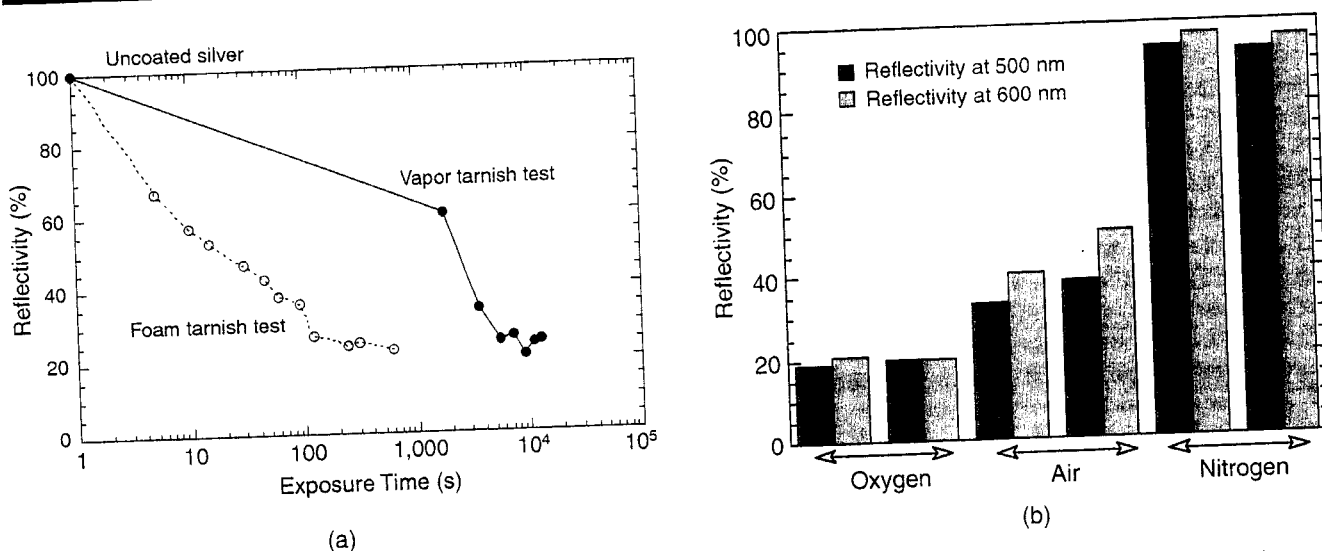

FIGURE 3. *The accelerated tarnish tests: (a) a schematic of the vapor tarnish test, and (b) a schematic of the foam tarnish test.*

slowly than the foam test. The foam test used a simpler solution but required constant attention throughout the test, and it produced an unpleasant odor when used in unventilated areas. The foam test also gave higher reproducibility than the vapor test. A common problem with the vapor test was nonuniform circulation of the vapors in the chamber, and this may have been the origin of its poorer reproducibility. The rate of corrosion in the foam test was strongly influenced by the nature of the carrier gas used to generate the foam. Figure 4(b) shows the effect of three different carrier gases (nitrogen, air, and oxygen) on the corrosion rate. It is evident from these data that oxygen plays a key role in accelerating the tarnishing process. Tarnishing was much slower in pure nitrogen, but it did still occur.

Figure 5 illustrates the proposed electrochemical model for the tarnishing of bare silver. Tarnishing occurs in the presence of H_2S and humidity. On the surface of silver, the H_2S molecules are reduced to sulfide anions and combine with silver cations. The presence of oxygen provides a fast cathodic reaction

(a)

(b)

FIGURE 4. *(a) The corrosion rate for the two accelerated tarnish tests on bare silver (filled circles represent the vapor test and open circles represent the foam test). (b) The tarnishing rate in the foam test was affected by the nature of the carrier gas that is used to generate the foam from the surfactant solution. The dark rectangles show the reflectivity measured at 500 nm, the light rectangles show the reflectivity at 600 nm, and the results are similar. In each case, the reflectivity was measured after 5 min of exposure to the sulfide foam.*
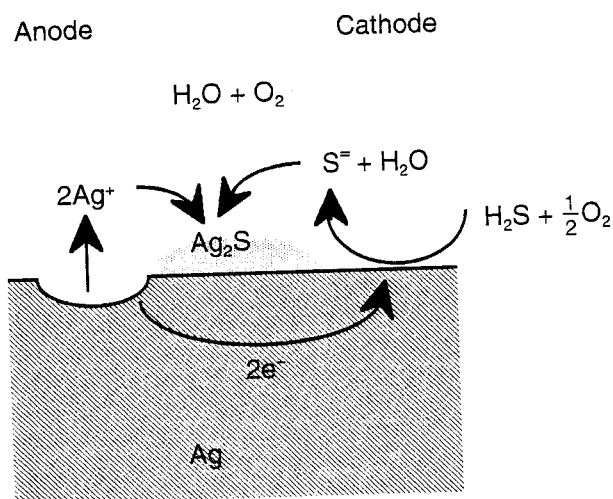
FIGURE 5. *An electrochemical model is envisioned for the tarnishing of silver. The anodic reaction is the silver oxidation, while the cathodic reaction is the formation of sulfide from H_2S and oxygen.*

for the generation of S^{2-}. In the absence of oxygen, the cathodic reaction would be the slower hydrogen evolution. Even if the silver surface oxidizes (or is oxidized), silver sulfide (Ag_2S) will still be formed via the double displacement reaction shown in Equation (5), which is spontaneous:

$$H_2S + Ag_2O \leftrightarrow Ag_2S + H_2O \qquad (5)$$
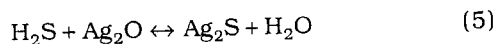
Optimizing the Time and Concentration of the H_2SO_4 Etch

The H_2SO_4 etch is a critical step prior to the deposition of the thiol layer. Figures 6 and 7 show

the percent reflectivity of silver samples as a function of the acid etch parameters. In each case, the SAM films were deposited by exposure of the cleaned and etched silver surface to a 10% hexadecanethiol solution for 10 min. Subsequently, the samples were placed in the vapor tarnish test for 24 h. Figures 6(a) and (b) show the dependence of the film quality on etch time for two different acid concentrations. Figure 6(a) shows data for concentrated H_2SO_4 and indicates an optimal etch time near 60 s. Figure 6(b) shows data for a 10% H_2SO_4 solution and reveals a peak in the film quality near a 5-min etch time. Figure 7 shows the effect of performing a 1-min etch with different concentrations of the H_2SO_4. The peak in the sample reflectivity occurred for a 10% H_2SO_4 solution, by volume. The data show that the dependence is flattened near the maximum. Operation of the acid etch near 10% H_2SO_4 reduces the dependence of the treatment on small errors in concentration and time. Unless stated otherwise, the 10% H_2SO_4 etch was used predominantly in this study.

Optimizing Alkane Chain Length

Several different lengths of thiols were tested early in the program of study. The optimum carbon length for resistance to tarnishing was found to be either C14 (tetradecanethiol) or C16 (hexadecanethiol). Table 1 shows the data from this study. The samples were placed in the vapor tarnish test until a notable discoloration (yellowing of the surface) was observed with the naked eye. The tetradecanethiol and hexadecanethiol films showed no discoloration after ~12 h. Longer time studies were not performed. Because the tetradecanethiol was more difficult to ob-
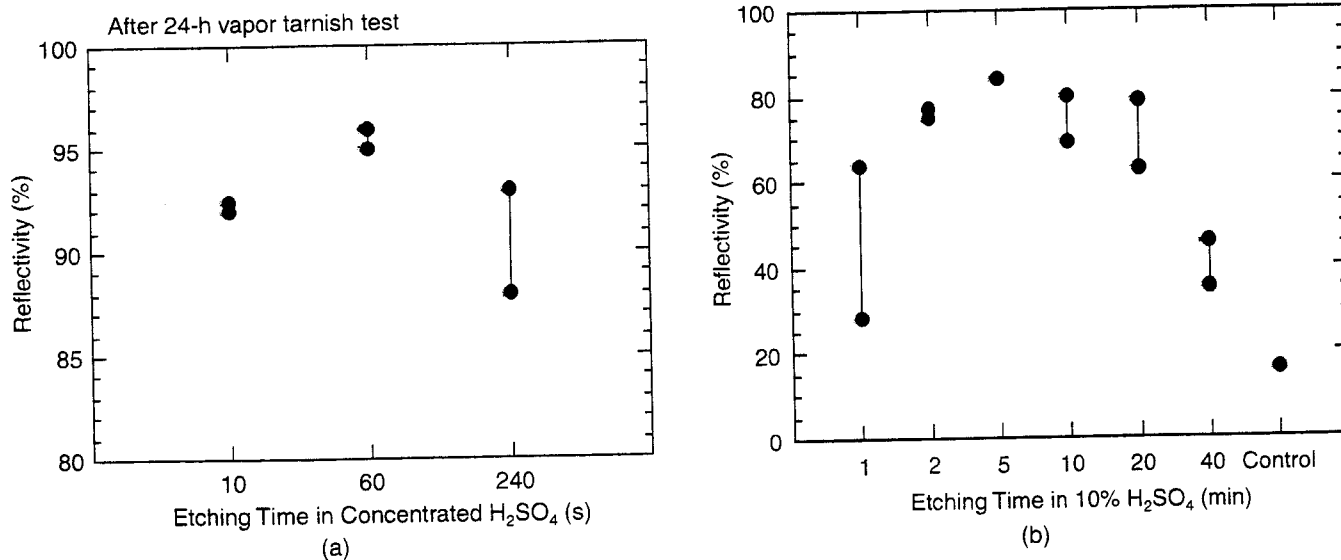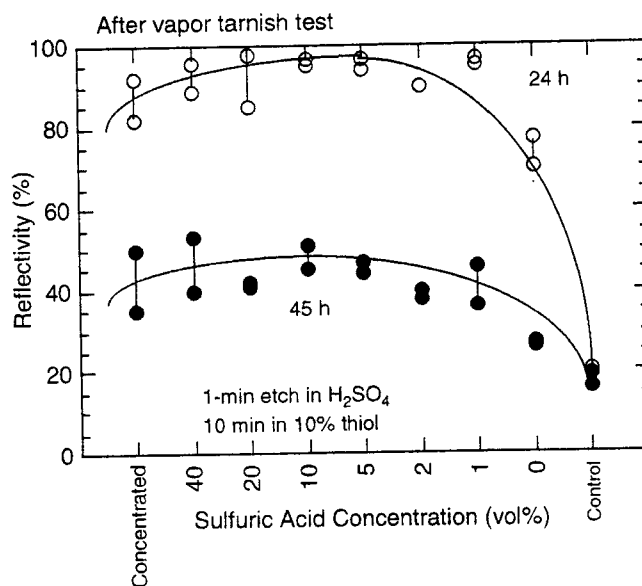
FIGURE 6. *The reflectance for: (a) silver samples that were etched for different times in concentrated H_2SO_4 and (b) samples that were etched for different times in a 10% H_2SO_4 solution. Each acid concentration exhibited a different optimum etching time. (After etching, the silver samples were coated for 10 min in 10% C16, and then exposed to the 24-h vapor tarnish test. The control was unetched, uncoated silver.)*

tain, research was conducted with hexadecanethiol films. Notably, Kartlücke, et al., also reported the best protection with C16.[18] The dependence of the film's barrier properties on chain length was also reported for copper[9] and gold.[3]

Optimizing Time vs Concentration of Thiol Deposition

Figure 8 displays the EIS data used to choose the optimum deposition times. These data show that optimum layers formed at 2 min to 4 min for 92% thiol (Figure 8[a]) and 30 min to 60 min for a 2% thiol solution (Figure 8[b]). These times correspond to the maximum impedance and phase angle in the EIS response. For the concentrated solution (Figure 8[a]), it is clear that the film formed on the surface within a few seconds of being placed in the thiol solution. Subsequently, there is an induction time for the film to optimize, and presumably the annealing of defects occurs during this time. At longer times the film quality degrades. For these exposures, the low-frequency impedance revealed the presence of pinholes, which presumably arose through corrosion. The dilute solution trials show an induction time for the film formation that is significantly longer than that for the concentrated solutions. As with the concentrated solution data, these trials revealed an optimum time for silver exposure to the solution. Other trials, not shown here, demonstrated good coatings for the 2% thiol even at 600 min of immersion, but these results were not always reproducible. The calculated thickness of the SAM coating varied from 2 nm (one monolayer) to 8 nm (4 monolayers). Often, there appears to have been excess thiol layers

FIGURE 7. *The peak reflectance for silver samples (etched for 10 minutes, thiol-coated 10 min in 10% C16, and 24-h vapor tarnish tested) is shown as a function of the H_2SO_4 concentration. The control was unetched, uncoated silver. The optimum H_2SO_4 concentration was ≈10 vol% H_2SO_4.*

on the surface, which could act as a reservoir to coat accidental scratches, as described by Kartlücke, et al.[18]

The SAM coating deposited by the 92% thiol for 2 min appeared to be identical to the SAM coating deposited by 2% thiol for 30 min. The water drop contact angles for these two coatings were 115 ± 3 degrees. In contrast, the bare silver surface gave a

TABLE 1
Comparison of Different Length
Thiol Chains to Tarnishing Resistance

Length of Thiol Carbon Chain	Hours to Discoloration
Uncoated	0.3
C5	0.5
C8	4.5
C12	9.0
C14	>11.5
C16	>11.5
C18	6.0

contact angle of 61 ± 3 degrees with water (Figure 9[a]). The reflectivity (at 500 nm) of the two samples after 5 min in the foaming tarnish test was 99 ± 1%. In contrast, a 5-min exposure of the bare silver surface to the foaming solution reduced the reflectivity to 20 ± 1% (Figure 9[b]).

In principle, it should be possible to define the optimal time-vs-concentration window for film formation. Figure 10(a) shows data that identify the optimum thiol concentration needed for a 10-min deposition time. The EIS data show a well-defined maximum in both the magnitude and the phase shift near a 7.5 vol% hexadecanethiol solution. Combining these data with the other reported data allows an optimum time-vs-concentration window to be sketched (Figure 10[b]). For immersion times that were too short for the concentration of the thiol, incomplete films were formed and their tarnish resistance was poor. For deposition times that were too long for the concentration of the thiol solution, the surface began to corrode from exposure, causing a reduction in the film's tarnish resistance. The data shown are for

silver surfaces. An optimum is expected for other materials as well, but the location of the time-vs-concentration window may shift.

Mechanism of Formation and Tarnish Protection

The hexadecanethiol is believed to react with the silver surface by the chemical bonding of the sulfur atom to a silver atom on the surface. The silver surface is therefore tarnished one-atom deep. The hydrocarbon tail that is bonded to the sulfur is oriented away from the silver surface, and this array of bonded molecules forms a one-molecule thick ordered layer known in the literature as a SAM.[3-20] The hydrocarbon layer is hydrophobic, repelling polar groups such as water (H_2O) and H_2S. Thus, the silver surface is made inert by the reaction with sulfur, the SAM barrier layer, and the repulsion of water and H_2S by the hydrocarbon tail. The corrosion or tarnishing rates are therefore significantly reduced.

Miscellaneous Observations

Hexadecanethiol has a high vapor pressure, and the vapor can disperse from an open vessel and coat surfaces in the vicinity. Uncoated silver samples placed in the same tarnish chamber as thiol-coated samples can become partially coated with thiols and exhibit reduced tarnishing rates. Care must be taken to prevent the thiol from also contaminating the glassware. Contaminated glassware can be cleaned with a bleach solution.

Removal of the hexadecanethiol SAM was accomplished by heating in air to vaporize/oxidize the coating. Pinholes began to develop in the coating after 30 min at 100°C, while complete vaporization/oxidation of the thiol occurred after 30 min at 150°C. Thiol-coated silver surfaces were easily joined with
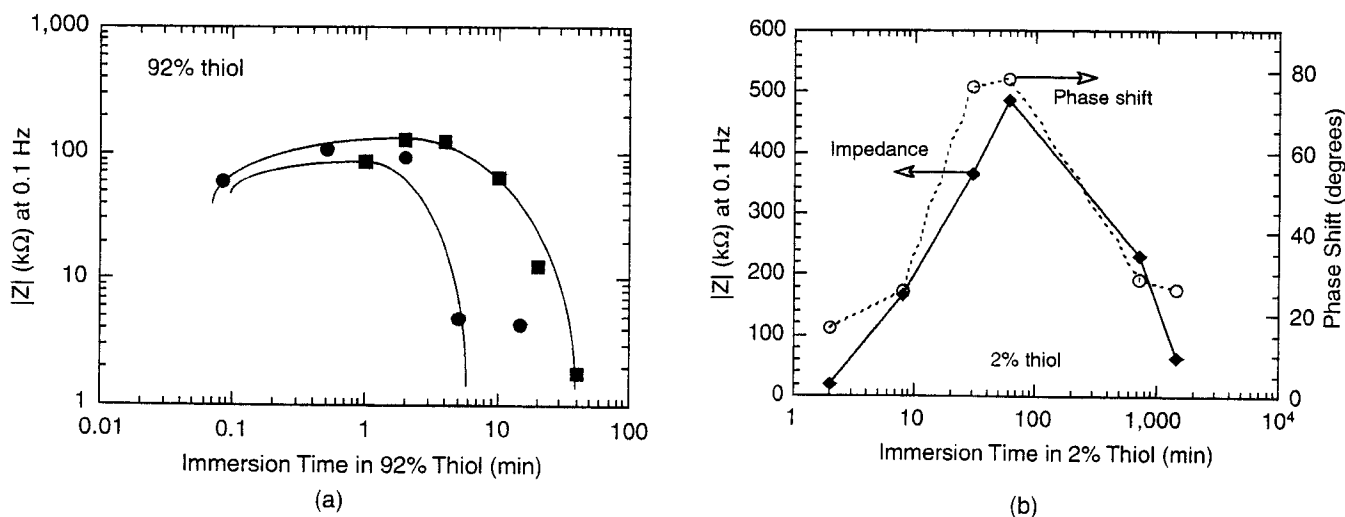
FIGURE 8. *(a) The maximum impedance for SAM films formed from a 92% hexadecanethiol solution as a function of the sample's immersion time in the solution (the different data points are for the different runs). (b) The maximum phase angle and impedance for SAM films formed from a 2% hexadecanethiol solution as a function of the sample's immersion time in the solution. For both solutions, there was an optimum immersion time.*

SAM and contact angle

(a)

SAM and reflectivity

(b)
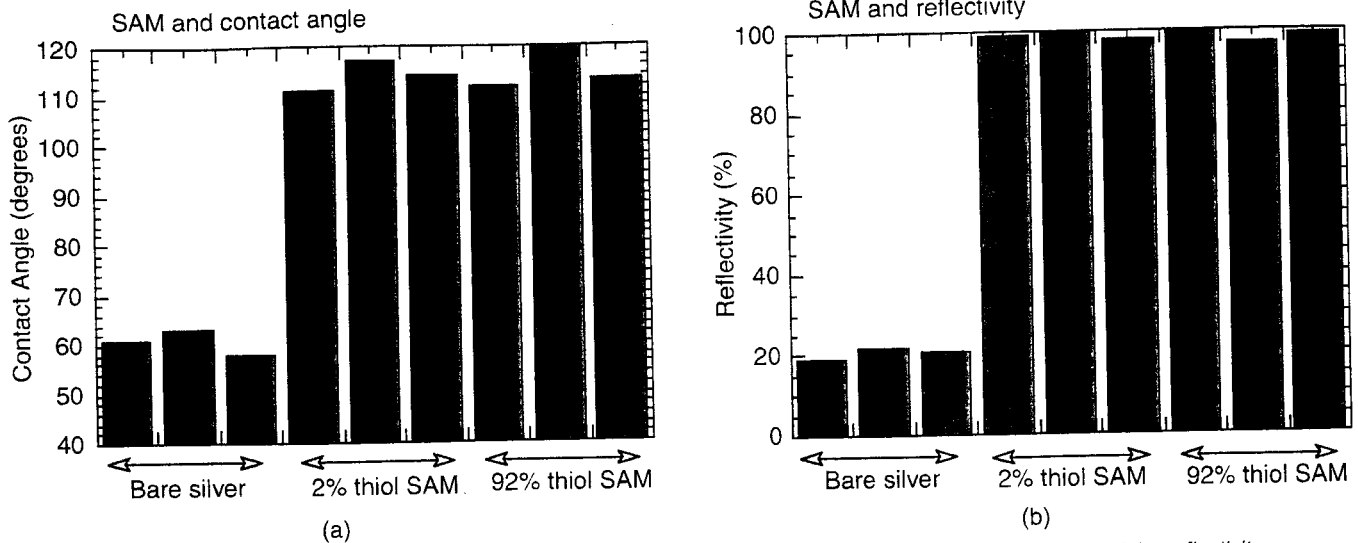
FIGURE 9. *Regardless of whether the film was formed with a 2% thiol or a 92% thiol, the contact angle and the reflectivity of the coated surfaces were similar.*

10-min thiol deposition time

(a)

Window for optimum coatings

(b)
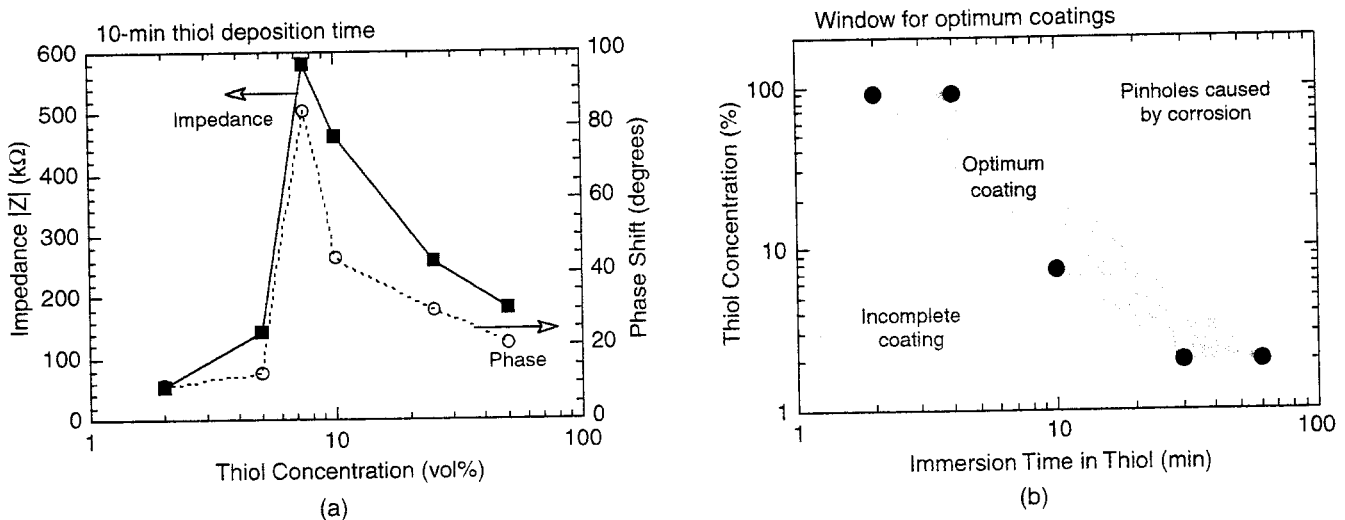
FIGURE 10. *(a) The phase shift and impedance for SAM films (exposed to hexadecanethiol solutions for 10 min) as a function of the concentration of the solution. (b) A sketch of the window of optimal times and concentrations for a monolayer film formation.*

lead-tin solder since the heat and/or the flux removed the thiol SAM.

Since the SAM tail is an oil/wax, it provided poor adhesion for glues or epoxy. Two-part epoxy from Devcon Corp. (2-Ton Clear[†]) showed a bond strength of only 5 psi to 10 psi after curing overnight. The thiol SAM could be removed by soaking for several minutes in a household bleach solution (5% NaOCl) or in 50% NaOH solution, but these solutions discolored the silver surface, turning it grayish-black. Small areas of the thiol SAM could be removed with a cotton swab soaked in bleach. The thiol-coated surface is a waxy surface and seems to yellow by picking up dust from the air. This yellowing can be easily re-

moved by washing the coated silver in warm soapy water using a soft cloth. However, this cleaned surface tarnished more rapidly.

The concentrated hexadecanethiol has a stench and is an irritant to the eyes, skin, and respiratory tract. The International Chemical Safety Card for 1-Hexadecanethiol is located on the World Wide Web.[24] The National Institute for Occupational Safety and Health (NIOSH) guidelines recommend 5.3 mg/m^3 as the 15-min exposure limit.[25] However, the hexadecanethiol SAM on a carefully rinsed surface was in minute quantities (2 mg/m^2 to 8 mg/m^2) and was not found to have an odor, nor did it irritate the skin or eyes.

CONCLUSIONS

❖ SAM films of alkanethiols were formed on silver, and the monolayer films provided resistance to atmospheric tarnishing without affecting the appearance of the silver. Accelerated tarnish tests were developed to test the tarnish resistance. EIS was used to optimize the surface preparation and the SAM deposition. The procedure for applying SAM to silver consisted of a four-step process: degreasing, acid etching, thiol deposition, and rinsing. The thiol deposition step varied from 2 min for a 92% thiol to 1 h for a dilute thiol solution.

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