

SILVER SULFIDATION KINETICS IN FLOWERS OF SULFUR ENVIRONMENT

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ABSTRACT

The susceptibility of silver to sulfidation attack has been a continuing issue for the reliability of surface mounted resistors exposed to sulfur-bearing atmospheres. New conformal coatings have been developed to protect these resistors when exposed to harsh environments. This paper will present data showing how the kinetics of silver sulfidation varies with temperature when exposed to a flowers-of-sulfur (FOS) environment. Examples of susceptible resistors failing in an FOS environment will also be presented as well as examples of how new types of conformal coatings can prevent sulfidation attack of silver.

Key words: Flowers-of-sulfur, silver sulfide, tarnish growth, conformal coatings, sulfidation corrosion.

BACKGROUND

Tarnishing of Silver

The tarnishing of silver when exposed to sulfur-bearing environments is a well-known phenomenon. The nature of the tarnish film has been studied for the last several decades, particularly with regard to what environmental variables affect the growth of the tarnish. For archival purposes, the goal was to determine which substances could tarnish silver artifacts in museums [1]. From an engineering point of view, an early goal was to understand how the tarnish film interferes with silver-plated electrical contacts[2]. The interest in understanding the latter issue was to improve the reliability of electrical equipment having silver-coated contacts when exposed to reduced sulfur species in the environment. In addition to silver contacts in switches, an understanding of how silver terminals in surface mount resistors was also sought. A review of how copper reacts with the contaminants in the environment, which has received a greater share of attention than tarnishing of silver, is a subject beyond the scope of this paper.

Previous investigators have found that the rate of tarnishing of silver in the field versus laboratory tests are different and a variety of growth rate kinetics have been reported for apparently the same sulfidation reactions. The source of the differences was likely the variety of reduced sulfur species

that can be found in the field compared to the ability of carefully controlling the sulfur environment in the laboratory [3]. However, even in carefully controlled laboratory settings, one early paper on silver tarnishing stated that “parabolic, cubic, and nearly linear growth rates have been reported for silver sulfide tarnish layers”[4]. These differences in growth rate kinetics have been attributed to whether the silver sulfide film grows as a continuous film or as a discontinuous film and whether the characteristic needle-shape silver sulfide crystals become the dominant morphological feature.

To provide a consistent environment for studying the tarnishing of silver, a flowers-of-sulfur environment was employed. Flowers of sulfur was used as the tarnishing agent for silver test coupons because it is easy to setup, safe to handle, and has relatively easy test equipment requirements compared to the use of hydrogen sulfide, which is the other common tarnishing agent used in laboratory tests.

EXPERIMENTAL

All the flowers of sulfur tests described in this paper were conducted in a modified vacuum oven that had an interior working volume of approximately one-half cubic foot. An external temperature controller, rather than the built in oven temperature controller, was used to more precisely control the oven temperature to ± 1 °C.

A Pyrex baking dish was used to hold the flowers of sulfur powder and a small stainless steel tube was used to serve as both a vent and support for hanging coupons and samples within the oven. A small 12 VDC muffin fan was used to help circulate the air within the oven to facilitate mixing of the sulfur vapor within the oven. Figure 1 is a photograph of the oven containing two silver coupons under test.

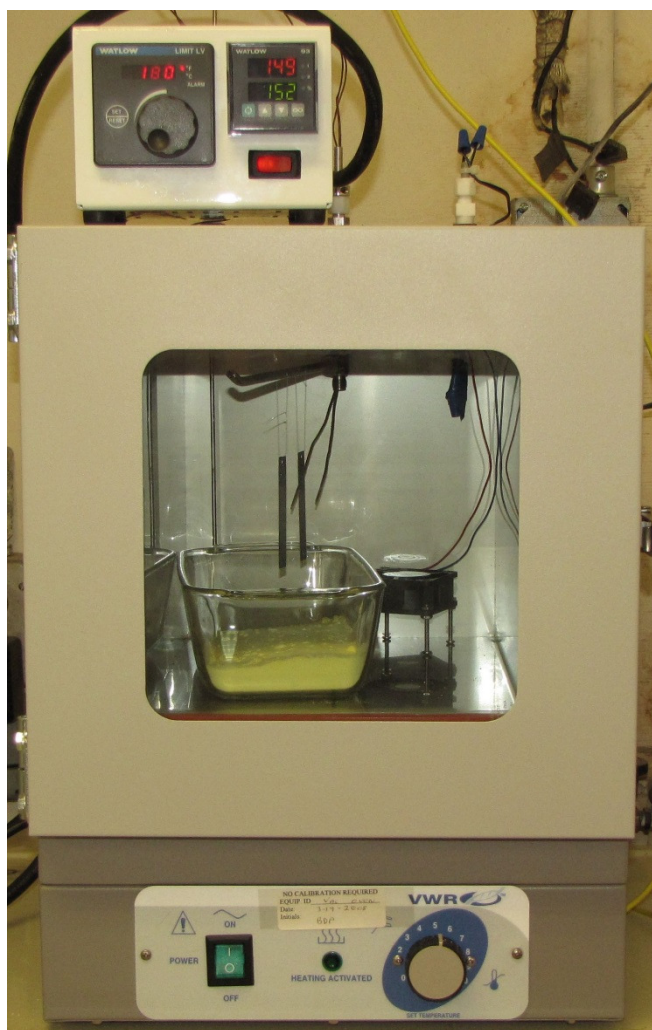


Figure 1. Photograph of modified vacuum oven used to conduct the flowers of sulfur tests.

All the silver coupons used for the kinetics study were cut from sheets with a nominal thickness of 0.020 inch. Final dimensions of the coupons were approximately 3 inches long and 0.5 inch wide. Holes approximately 1/16th inch in diameter were punched on both ends of the coupon to facilitate suspending them in the test chamber. The purity of the silver was 5N or 99.999 percent.

Prior to testing, the surfaces of the coupons are lightly ground using 400 grit followed by 600 grit sandpaper to remove any surface contamination. The coupons are then cleaned in boiling reagent acetone and boiling reagent isopropyl alcohol (IPA). After cleaning, the coupons are weighed on an analytical balance having a precision of 0.01 mg. Figure 2 is a photograph showing a typical silver coupon prior to testing.

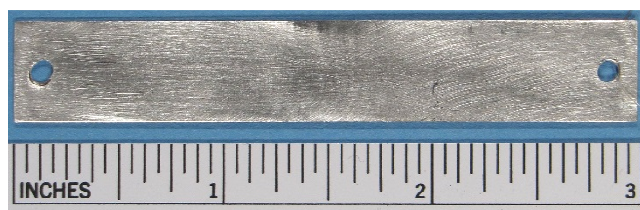


Figure 2. Photograph of typical silver coupon prior to testing in the flowers of sulfur chamber.

Silver Sulfide Film Thickness Measurements

The procedure for measuring the silver sulfide film thickness consisted of exposing a minimum of two and up to four replicate coupons in the chamber and periodically removing them for weighing. It was known from previous studies that the predominant silver sulfide compound that forms when exposed to reduced sulfur vapor species is acanthite, the monoclinic form of Ag₂S[5, 6]. In light of this information, it was felt not necessary to use coulometric reduction[7], which is often used to both measure thin-film thicknesses of tarnish on silver and also used to identify other atmospheric corrosion products of silver such as silver chloride or silver oxides. Neither of the latter two compounds was detected when only flowers of sulfur was used at the corrodent. The weight gain data was used to calculate the silver sulfide film thickness using the following equation:

$$D = \frac{\Delta w}{\rho_{Ag_2S} \cdot A} \cdot 7.728 \cdot 10^7 \quad \text{Eqn. 1}$$

Where D = Film thickness in nanometers,

Δw = Coupon weight gain in grams,

ρ_{Ag_2S} = Density of silver sulfide (7.23 g/cm³)[8],

A = Surface area of coupon (19.35 cm²).

7.728 is the ratio of the molecular weight of Ag₂S to S.

The silver coupons were suspended in the chamber using four-pound monofilament fishing line made from fluorocarbon and having a nominal diameter of seven mils or 0.18 mm. The coupons were periodically removed from the chamber, weighed and then returned to the chamber for additional exposure. The coupons were carefully handled to prevent any silver sulfide crystals from falling off the coupon during the weighing process. Previous experience has shown that the silver sulfide coating is very tenacious and not easily dislodged until the crystals become relatively long. The humidity of the chamber was not controlled and measurements at 60° C using a digital hygrometer indicated that the relative humidity in the chamber was no greater than 20 percent. In any case, the relative humidity was judged not to be a factor in the sulfidation rate of the silver because other studies have shown that it does not play role in the silver sulfidation rate[9].

Conformal Coatings

Two types of test coupons were used to evaluate the performance of candidate conformal coatings; namely silver coated glass slides and circuit boards, the latter containing 25 chip resistors. The glass slides have been described elsewhere[10] but are presented here again for completeness. The glass slides were standard microscope slides approximately 3 inches long and 1 inch wide. The slides were coated with approximately 1 micron of silver using e-beam evaporation techniques. The silver was etched into a serpentine pattern to provide a nominal resistance of 5.5 ohms. A completed silver test slide wired for 4-wire resistance measurements is shown in Figure 3.

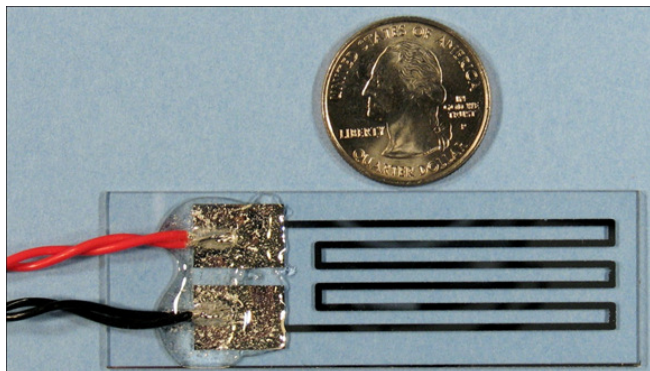


Figure 3. Photograph of glass slide with pure silver traces used in conformal coating evaluations.

The chip resistors used on the boards were 1%, 1/8th watt, 10k Ω , 0805 type surface mounted resistors. A particular manufacturer of these resistors was selected because prior experience indicated that their chip resistors were susceptible to sulfidation. The resistors were soldered to circuit boards, using lead/tin solder, in a parallel-circuit pattern to allow automated collection of resistance data using a data acquisition system (DAS). An example of a board containing the chip resistors is shown in Figure 4.

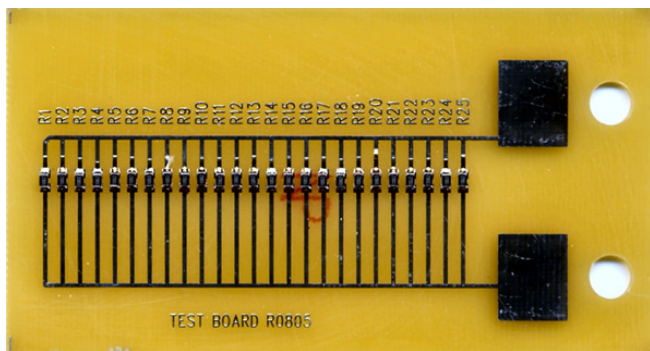


Figure 4. Printed circuit board showing 25 chip resistors soldered in a parallel circuit arrangement.

Six silver coated glass slides and three chip resistor boards were coated with a proprietary conformal coating. The coating thicknesses on the boards and resistors were varied to determine if the different thicknesses provided different levels of protection to sulfidation. Table 1 lists the sample type and relative coating thicknesses that were applied to the

test articles by HzO, Inc. These coatings ranged in thickness between 4 and 12 microns. In addition, a control chip resistor board was tested that had a standard silicone conformal coating (Dow 4097) applied to it. The silicone coating thickness was approximately 51 microns (2 mils). An uncoated silver coated glass slide was also tested for purposes of comparison.

Resistance values of all the samples were monitored during their chamber exposure using the 4-wire resistance method and a data acquisition system was programmed to collect data every 15 to 30 minutes.

Table 1. Test sample type and relative coating thickness

Test Sample Type	Sample Code	Coating Thickness (μm)
Chip Resistor	223	low
	323	medium
	423	high
	Coating Control	51
Silver Coated Glass Slides	221	low
	222	low
	321	medium
	322	medium
	421	high
	422	high
	Silver Control	none

DISCUSSION OF RESULTS

Sulfide Growth Kinetics on Silver Coupons

At the time of this writing, the kinetics of silver sulfide formation at three temperatures were being examined, namely 50 °C, 65 °C, and 80 °C. Data for approximately 31 day (750 hours) were collected at each temperature. The graph of the sulfide film thickness calculations versus time for the three different temperatures is shown in Figure 5. The error bars on the graphs represent the minimum and maximum values of the replicate coupons.

The dependency of film thickness versus time is less than linear for all three temperatures over the course of the 750-hour test. However, if only the first few days of testing are examined, it can be seen that the dependency can be closely fitted to a linear dependency, which likely explains why some researchers assumed this dependency held for longer times. Linear dependency occurs when the film formation is quite thin and not diffusion limited.

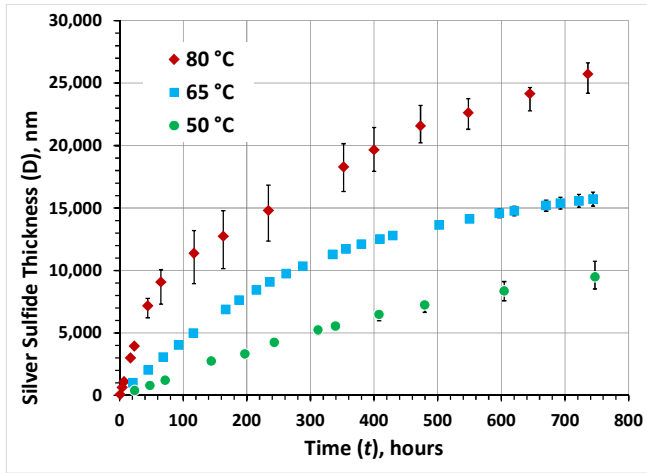


Figure 5. Graph of silver sulfide film thickness versus time at 50 °C, 65 °C and 80 °C.

Figure 6 shows the linear fits (dashed lines) of the data presented in Figure 5 for relatively early exposure times, namely less than 150 hours.

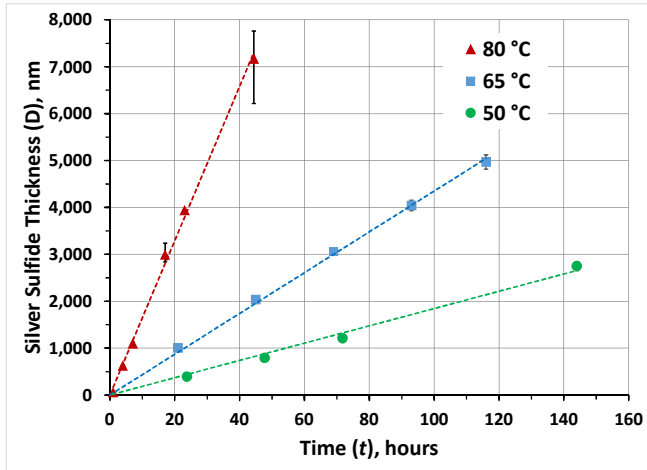


Figure 6. Linear trend lines for silver sulfide versus time for less than 150 hours for 50 °C, 65 °C and 80 °C exposures.

The equations for the linear regression lines shown in Figure 6 along with their R-squared values are the following:

$$50\text{ }^{\circ}\text{C}: D = 18.437t, R^2 = 0.9902$$

$$65\text{ }^{\circ}\text{C}: D = 43.499t, R^2 = 0.9976$$

$$80\text{ }^{\circ}\text{C}: D = 164.567t, R^2 = 0.9975$$

Where D is the silver sulfide thickness in nanometers and t is exposure time in hours.

When the film thickens, the traditional diffusion-limited parabolic growth model predominates. For the lowest tested temperature of 50 °C, the parabolic model fits the data quite well for the entire 750-hour exposure but the model begins to break down for long exposures at the higher test

temperatures of 65 °C and 80 °C. Figure 7 shows the graph of the parabolic fits (dashed lines) for all the data. As can be seen, the parabolic regression line is beginning to turn downward at the highest exposure period for 65 °C and 80 °C.

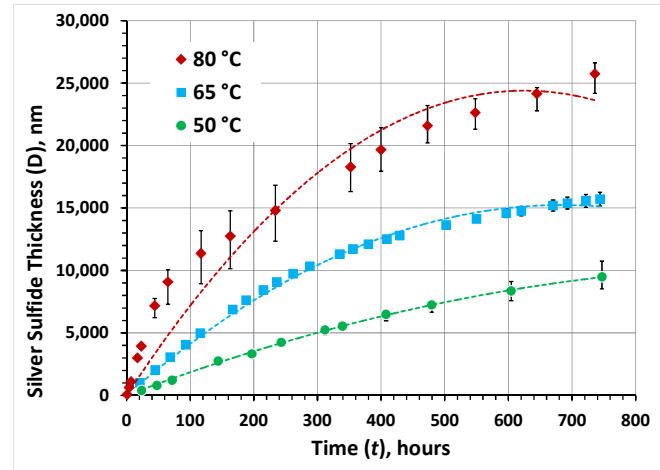


Figure 7. Parabolic trend lines for silver sulfide versus time for all the data of the 50 °C, 65 °C, and 80 °C exposures.

The equations for the parabolic regression curves shown in Figure 7 along with their R-squared values are the following:

$$50\text{ }^{\circ}\text{C}: D = -0.0091t^2 + 19.437t, R^2 = 0.9990$$

$$65\text{ }^{\circ}\text{C}: D = -0.0325t^2 + 44.521t, R^2 = 0.9952$$

$$80\text{ }^{\circ}\text{C}: D = -0.0625t^2 + 78.103t, R^2 = 0.9456$$

As discussed by Bennett et al. [4], the growth rate can increase again when the formation of silver sulfide “needles provide easy diffusion channels for the reactants through the thick tarnish layer.”[4]. This later stage is more likely to occur at the highest test temperatures and extended exposure times. Figure 8 is a graph for 65 °C and 80 °C at exposure times beyond 350 hours along with a cubic regression line. These trend lines clearly show a much better fit than for the parabolic regression lines at the longer exposure times. While not shown, the cubic regression line fits for all the data points of the 65 °C and 80 °C data

The equations for the cubic regression curves fitted to relatively long exposure times (Figure 8) along with their R-squared values are the following:

$$65\text{ }^{\circ}\text{C}: D = 3.35 \times 10^{-5}t^3 - 0.0668t^2 + 52.33t, R^2 = 0.9995$$

$$80\text{ }^{\circ}\text{C}: D = 5.19 \times 10^{-5}t^3 - 0.102t^2 + 81.57t, R^2 = 0.9976$$

As can be seen, these fits are better than the parabolic regression curves shown in Figure 7.

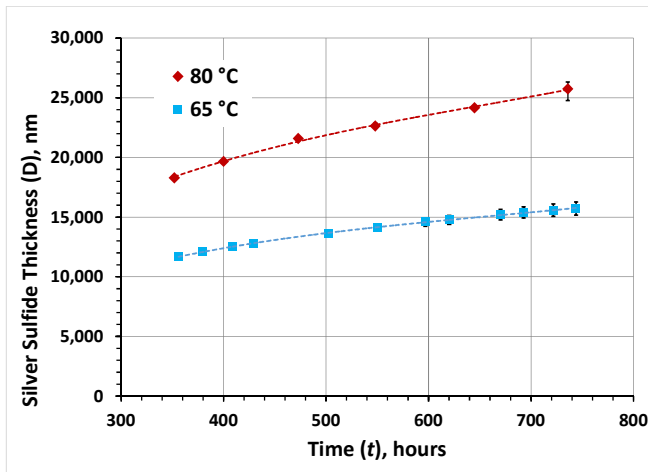


Figure 8. Cubic trend lines for silver sulfide versus time for exposures greater than 350 hours for the 65 °C and 80 °C temperatures.

Film Thickness as a Function of Time and Temperature

While growth data for specific temperatures is helpful, the goal is to arrive at an equation that will provide film thickness for any reasonable temperature and time duration. One equation covering the range of linear, parabolic, and cubic behavior for silver sulfide growth may not be possible but for the linear region, an equation can be derived based on the data in Figure 6. Figure 9 is a graph of the slope of the linear behavior versus temperature.

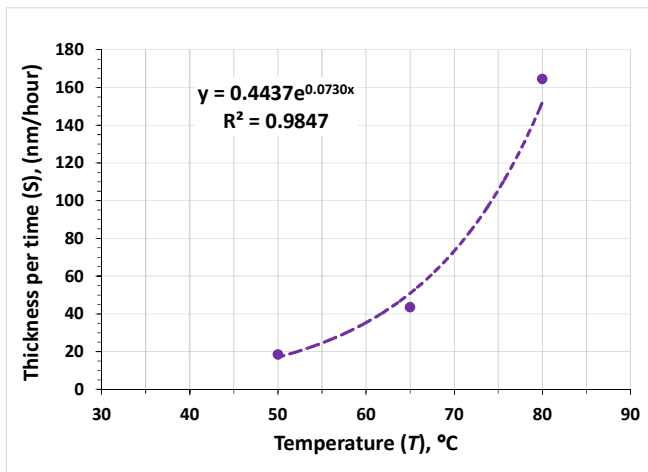


Figure 9. Exponential curve fit to the linear slopes versus temperature data for silver sulfide thickness.

Based on the best fit to the slopes, the following equation provides a reasonable agreement with experimental data.

$$D = 0.4437 \cdot t \cdot e^{0.073 \cdot T} \quad \text{Eqn. 2}$$

Where D = Silver sulfide film thickness in nanometers,
 t = time in hours,
 T = temperature in °C.

This range of validity for this equation is bounded by the experimental data shown in Figure 6.

Silver Sulfide Crystal Morphology

Examples of the formation silver sulfide crystal needle formation on silver coupons are shown in Figures 10 and 11. The condition required to grow crystals to this extent was an exposure for 800 hours at a temperature of 60 °C. It is speculated that these leaf or needle-like crystal serve as channels for allowing sulfur vapor to reach the silver substrate without having to diffuse through the silver sulfide film itself. The sulfur is also adsorbed onto the dendritic crystals that result in the lengthening of the crystals. A detailed description of the silver sulfide dendritic crystal growth mechanism is presented by Kasukabe[6]. It should be noted that the dendritic growth mechanism of Kasukabe does not account for the total average silver sulfide film thickness presented in this paper.

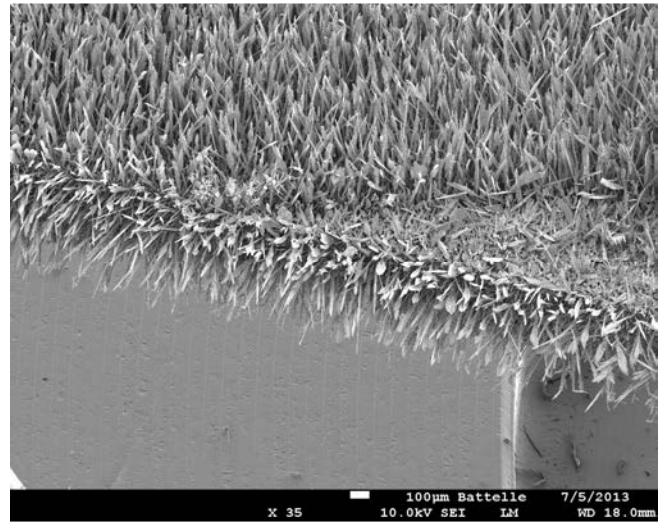


Figure 10. Scanning electron micrograph of silver sulfide crystals that formed on a silver coupon at 60 °C over 800 hours.

It seems reasonable, based on the above analyses, that several mechanisms controlling the growth rate of silver sulfide occur on silver coupons as exposure times increase. During the first or linear phase, the silver sulfide forms uniformly on the silver coupon and the film thickness grows linearly. The transport of sulfur vapor to the silver surface become diffusion limited as the film thickens. During this time, the film growth begins to follow parabolic behavior. Concurrent with the thickening film, needle shaped crystals begin to form on nucleation sites and exhibit the morphology shown in Figures 10 and 11. The transport of sulfur to the surface along the dendrites and the growth of the dendrites themselves contribute to a slight increase in silver sulfide growth rate that appears to follow a cubic rate dependency.

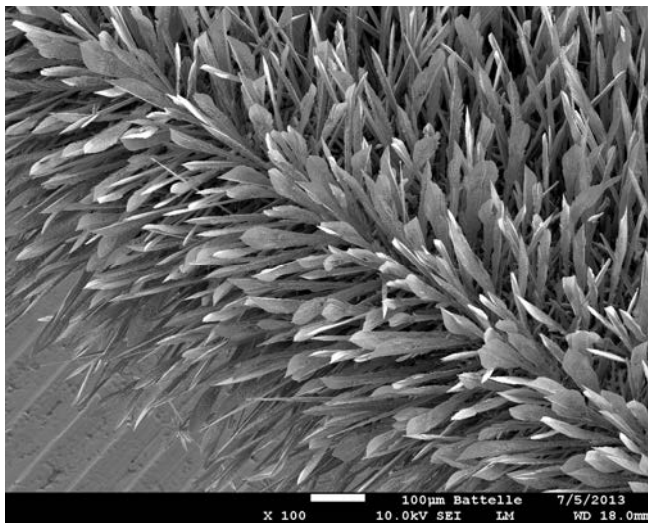


Figure 11. Higher magnification view of surface shown in Figure 10.

Coated Slides and Chip Resistors

The initial test temperature of the chip resistors and silver coated glass slides was maintained at approximately 60 °C. After approximately 17 hours, the uncoated silver glass slide control sample completely failed by converting its entire exposed silver to silver sulfide. The other coated samples, however, exhibited essentially no change after several hundred hours of testing. To assist in the acceleration of the silver sulfide growth, the test temperature was increased to approximately 71 °C after 500 hours of testing. When this was done, the chip resistors under the silicone conformal coating began to fail on an almost daily basis. At the completion of the 1080-hour test, 23 of the 25 chip resistors on the control board had failed. Moreover, the silver under coatings 221 and 222, which had the thinnest coating, began to exhibit relatively large increases in resistance with exposure time. The silver under the other coating codes, however, exhibited measureable though significantly less resistance change with time.

Figures 12 to 14 show charts of the resistance versus time of the coated chip resistor boards and the silver coated slides. The silver coated slides appear to show the most sensitivity to small changes in sulfidation resistance whereas the resistance of the chip resistors exhibited abrupt changes as the result of the entire chip resistor failing. The data clearly shows that the medium and high thickness proprietary coatings provide protection to its silver substrate for at least 1,300 hours in flowers of sulfur environment at elevated temperature. The lower thickness conformal coating was too thin to prevent sulfide formation at elevated temperatures.

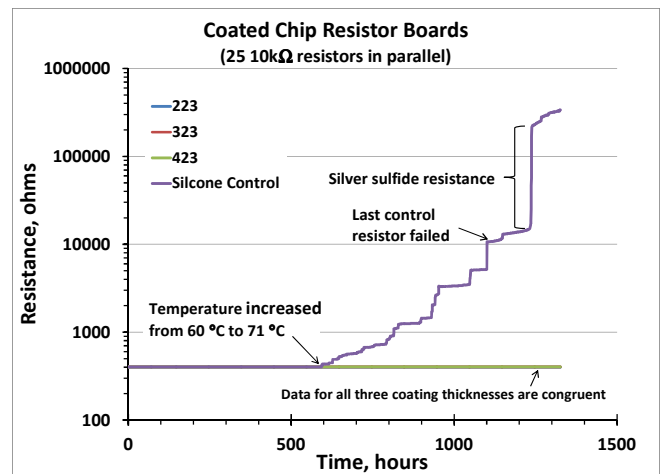


Figure 12. Change in resistance versus time for 25 chip resistors in parallel as they are exposed to the flowers of sulfur environment from 60 °C to 71 °C.

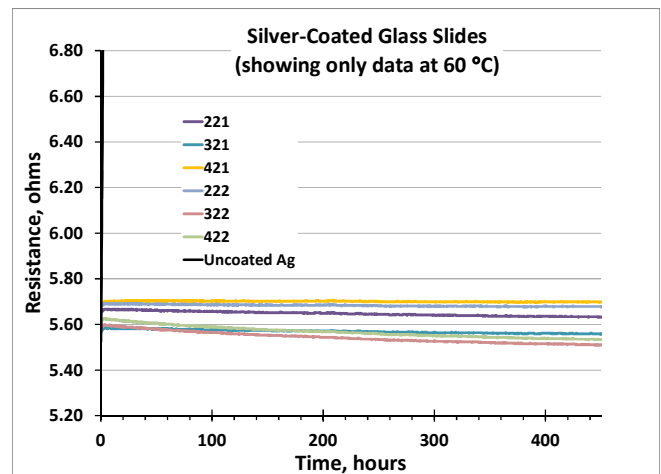


Figure 13. Change in resistance versus time for silver-coated glass slides coated with proprietary coatings and exposed to the flowers of sulfur environment at 60 °C.

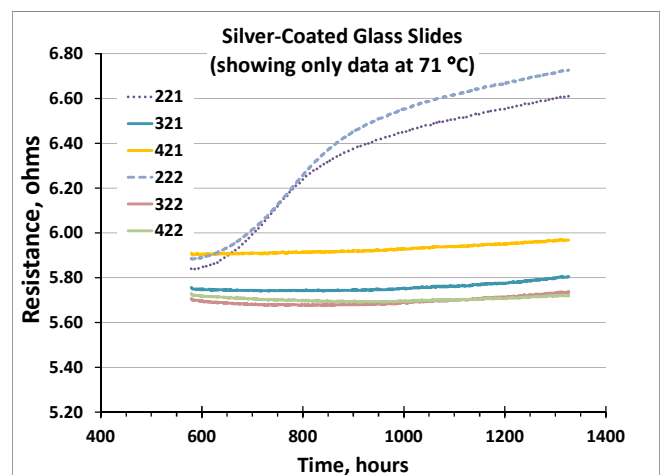


Figure 14. Change in resistance versus time for silver-coated glass slides coated with proprietary coatings and exposed to the flowers of sulfur environment at 71 °C.

CONCLUSIONS

Silver sulfide growth kinetics on silver coupons appears to follow three different growth mechanisms depending on the thickness of the film. Linear growth rate occurs early in the tarnishing process where silver sulfide is uniformly formed across the exposed silver surfaces; parabolic growth occurs when access to the silver substrate by sulfur vapors is diffusion limited by the thickening silver sulfide film; and cubic growth rate occurs when the dendritic sulfide crystals assist the transport of sulfur to the silver substrate. A silver sulfide growth rate equation derived for the linear behavior of the film growth accurately predicted the film thickness for that regime.

Proprietary transparent conformal coatings were developed to prevent the formation of silver sulfide. Coating on the low end of the specific range was not sufficient to prevent sulfide formation on the silver sputtered glass slides. Medium to high conformal coating thicknesses were required to prevent sulfide formation for at least 1,300 hours when exposed to a flow of sulfur atmosphere at 71 °C for the silver sputtered glass slide testing.

FUTURE WORK

Additional intermediate test temperatures and temperatures below 50 °C and above 80 °C will be conducted to refine and extend range of validity of the film growth kinetics equations.

ACKNOWLEDGEMENT

The authors would like to thank W.H. Abbott for valuable discussions and his review of data regarding silver sulfide thickness measurements and Ernie Patterson for his assistance in assembling the flow of sulfur chamber.

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