Failure Mechanism Analysis and prevention of Silver Electrode Corrosion

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Abstract. In this paper, the failure mechanism of sulfide corrosion of a batch of silver electrodes was studied by means of environmental simulation test, scanning electron microscopy (SEM), energy spectrum analysis (EDS), micro-CT, infrared spectroscopy analyzer(FTIR), pyrolysis gas chromatography mass spectrometry (Py-GC-MS) and specific surface area (BET) analysis. The results showed that the H\textsubscript{2}S in the air entered the silver electrode surface through the rubber by the adsorption and permeation effects, and corroded the silver electrode. What’s more, The change of pore size in silicone rubber will affect the H\textsubscript{2}S corrosion reaction. The smaller the pore, the higher the specific surface area and the more polar H\textsubscript{2}S molecules adsorbed by rubber. So the special pore distribution of the size of the intercalation was beneficial to reduce the diffusion resistance of H\textsubscript{2}S molecules in rubber. The above analysis results also provided ideas and direction for the improvement of silicone rubber. The pore distribution of silicone rubber could be controlled by controlling the viscosity and the surface drying time of the glue solution, so as to ensure the filling effect of the silicone rubber and prevent the corrosion failure of the silver electrode.

1. Introduction

Most metal materials are easy to react with sulfur compounds to form sulfides in the atmospheric environment, among which silver is the fastest [1]. Therefore, silver-containing electronic components, such as silver electrodes, are easy to undergo vulcanization reaction. The sulfurized electronic components will cause poor contact of circuit board, ion migration, open circuit and other phenomena, thus causing component failure and affecting service performance [2].

In order to avoid vulcanization reaction of electronic components, encapsulation glue is often used for sealing. Silicone rubber is a kind of commonly used encapsulation glue. Silicone rubber is a kind of linear polymer. The main chain is composed of alternating arrangement of silicon atoms and oxygen atoms. The side chain is symmetrical methyl and the two sides are hydroxyl groups[3]. The main chain structure of silicon oxygen alternation determines the macro flexibility of the material. Due to the high bond energy of silicon oxygen bond, silicone rubber has high thermal stability and excellent ozone aging resistance, electrical performance and biological adaptability [4]. Therefore, silicone rubber with high thermal conductivity is usually used in electronic products to solve the problems of sealing and heat dissipation of electronic components.

In this paper, basing on the failure of a silver electrode on a circuit board of a product, by means of SEM, EDS, micro-CT, FTIR, Py-GC-MS, BET and environmental simulation experiments, the specific reasons of the failure were analyzed, and the relationship between different batches of silver...
electrodes and different degrees of corrosion was studied. Finally, the failure mechanism of sulfide corrosion of silver electrode was established, and the corresponding solutions and preventive measures were put forward.

2. Phenomenological Analysis of the Failure of Silver Electrode

During the use of an electronic product, the circuit board was short circuited, and the failure reason was confirmed to be the failure of silver electrode through analysis. The internal microstructure of silver electrode was analyzed by micro-CT, and the internal microstructure of intact silver electrode and failed silver electrode was compared, as shown in Fig. 1. It can be seen that there are holes on the surface of the failed silver electrode, and the holes in the serious area have expanded into gaps.

![Micro-CT image of silver electrodes](image)

**Figure. 1** Micro-CT images of silver electrodes: (a) intact silver electrode (b) failed silver electrode.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to analyze the failed silver electrode. The analysis results are shown in Fig.2 and Table 1 respectively.

![SEM morphology and energy spectrum](image)

**Figure.2** SEM morphology and energy spectrum of electrode failure.

| element | Weight Percentage | Atomic Percentage |
|---------|-------------------|-------------------|
| C       | 22.42             | 45.43             |
| O       | 23.62             | 35.93             |
| Si      | 3.20              | 2.77              |
| S       | 8.26              | 6.27              |
| Ag      | 42.51             | 9.59              |

**Table 1. EDS analysis results of electrode failure.**

It can be seen from Fig. 2 and table 1 that sulfur and oxygen elements appear on the surface of
silver electrode. $\text{Ag}_2\text{S}$ layer and $\text{Ag}_2\text{O}$ layer are formed on the surface of silver electrode. While the resistance of $\text{Ag}_2\text{O}$ ($10^{-4} \, \Omega \text{m}$) is far less than the resistance of $\text{Ag}_2\text{S}$ ($10^{-10} - 10^6 \, \Omega \text{m}$) [5], so the effect of $\text{Ag}_2\text{O}$ on the resistance can be ignored. Since the corrosion product $\text{Ag}_2\text{S}$ will not form a dense protective film similar such as $\text{Al}_2\text{O}_3$ on the surface of Ag electrode, the corrosion reaction will be carried out all the time. According to Kim's research, the corrosion rate of silver in $\text{H}_2\text{S}$ environment depends on the content of oxygen and water. At the beginning, $\text{H}_2\text{S}$ was only adsorbed on the surface of silver, and did not react directly to form silver sulfide. $\text{H}_2\text{S}$ and oxygen react with silver to form silver sulfide. Water plays a role of carrier in the proton transfer reaction, so the increase of oxygen content and water content can accelerate the corrosion of silver [6-8]. Therefore, it was preliminarily determined that the failure of silver electrode was due to the corrosion reaction of $\text{H}_2\text{S}$, oxygen and water in the air with silver to generate $\text{Ag}_2\text{S}$, and the gradual thickening of $\text{Ag}_2\text{S}$ layer led to the failure of the circuit.

3. Simulation Experiment of $\text{H}_2\text{S}$ Corrosion Environment

In order to further investigate whether there are gaps in the electrode or the influence of welding process on the electrode, and to verify the corrosion phenomena of $\text{H}_2\text{S}$ in the air on the silver electrode, the simulation experiment of $\text{H}_2\text{S}$ corrosion environment was designed. The paper used the $\text{H}_2\text{S}$ gas generated after the reaction of ferrous sulfide and dilute sulfuric acid to react with the silver electrode. The selected silver electrode test samples are shown in Table 2.

| NO. | Sample Information                                      | Number |
|-----|---------------------------------------------------------|--------|
| 1   | Not welded after delivery                              | 2      |
| 2   | Normal reflow welding                                  | 2      |
| 3   | Weld according to the recommended reflow curve         | 2      |
| 4   | Reflow welding time above 220 °C for 1min              | 2      |
| 5   | After normal reflow welding, carry out three proofing coating | 2      |
| 6   | Soldering iron welding(260 °C, 1min)                   | 2      |
|     | Total                                                   | 12     |

The simulation test device is shown in Fig. 3. A brown glass wide mouth bottle was used as a test container. Put a culture dish with a diameter of 50 mm at the bottom of the wide mouth bottle, containing 20 ml 5% dilute sulfuric acid. Then weighed 8.8mg of ferrous sulfide and put it into a small weighing bottle, and placed it on the inside of the edge of the culture dish. Placed the numbered electrodes on the bottom of the test container in sequence. After the test container was closed, the container was shaken gently, so as to obtain the required $\text{H}_2\text{S}$ gas atmosphere of $50 \times 10^{-6}$ concentration. The test was stopped after 132 h. The morphological changes of the electrode were observed and the resistance value was measured.

![Figure 3. Simulation test device.](image-url)
The results showed that the surface of silver electrodes were blackened in different degrees. At the end of 132 h test, the contact resistance value after the test increased 400 times on average compared with that before the test. Sample 6 (260 °C, 1min) with poor welding conditions was observed under the micro-CT equipment. Compared with other electrodes, there was no obvious sign of severe corrosion, as shown in Fig. 4.

![Figure 4. Micro-CT images of (a) sample 1 and (b) sample 6 after test.](image)

The SEM and EDS were performed on the silver electrode after the test. The results were shown in Fig. 5 and table 3. Compared with the failed electrode (Fig. 2), the surface morphology and element content were basically the same.

![Figure 5. SEM morphology and energy spectrum of electrode after test.](image)

**Table 3. EDS analysis results of electrode after test.**

| element | Weight Percentage | Atomic Percentage |
|---------|-------------------|-------------------|
| C       | 23.07             | 48.30             |
| O       | 20.32             | 31.94             |
| Si      | 1.84              | 1.65              |
| S       | 9.69              | 7.60              |
| Ag      | 45.07             | 10.51             |

The above test results showed that the exposed silver electrode was easy to react with H₂S and generate sulfide. And the welding process will not cause serious damage to the electrode, leaving the silver electrode exposed to the sulfur environment and corroded.
4. Analysis of Corrosion Causes

How $\text{H}_2\text{S}$ enters into the circuit board to corrode the silver electrode? Firstly, the composition analysis of silicone rubber is needed to determine the content of sulfur element. Two facial silicone rubbers and two bottom silicone rubbers, numbered 1#, 2#, 3# and 4# respectively, were scanned by FTIR to analyze the general chemical composition of the sample. The main composition and the content of each element of the sample were found by Py-GC-MS.

The infrared spectrum is shown in Fig. 6. The main component of silicone rubber is polydimethylsiloxane. The element content of each sample obtained by Py-GC-MS is shown in Table 4.

![Infrared spectrum](image)

**Table 4.** The elements content of silicone rubbers 1# to 4#.

| NO. | S[\%] | Si[\%] | Na[\%] | Al[\%] | Fe[\%] | Ti[\%] |
|-----|-------|--------|--------|--------|--------|--------|
| 1#  | 0.18  | 24.55  | 0.0094 | 0.003  | 0.013  | 0.012  |
| 2#  | 0.17  | 24.94  | 0.0038 | 0.003  | 0.012  | 0.013  |
| 3#  | 0.065 | 26.98  | 0.011  | 0.001  | 0.015  | 0.012  |
| 4#  | 0.064 | 26.94  | 0.017  | 0.002  | 0.018  | 0.011  |

By comparing the element contents of the four samples, the contents of S, Si and Na were significantly different. The Si content of 1# and 2# was smaller than that of 3# and 4#. The reason may be that the content of siloxane is small, which should be the fluctuation of the quality of different batches of silicone rubber. The S content of 1# and 2# was significantly higher than that of 3# and 4#. It can be seen that the S content of facial silicone rubber was higher, which should be caused by the S content attaching to the surface before curing. The Na content of 1# and 2# was less than that of 3# and 4#, due to the effect of Na on the surface layer of silicone rubber to prevent the corrosion of silver electrodes.

According to the above test results, the reasons why $\text{H}_2\text{S}$ can corrode the silver electrode inside the silicone rubber are analyzed as follows:

1. Since the surface of the silver electrode cannot be completely fitted in the welding process, the air in the gap can provide $\text{H}_2\text{S}$, oxygen, water and other components at the beginning of the corrosion reaction.

2. Adsorption of $\text{H}_2\text{S}$ by silicone rubber. Because silicone rubber is a porous material with a large surface area. The hydroxyl group on the surface has a certain degree of polarity, so it can preferentially adsorb polar molecules, such as $\text{H}_2\text{O}$ and $\text{H}_2\text{S}$.

3. Penetration of $\text{H}_2\text{S}$ in silicone rubber. The basic structural particle of silicone rubber is Si-O tetrahedral system, and the framework of silicone rubber is formed by Si-O tetrahedral stacking [9,10]. The space in the particles during stacking can be regarded as the pores of silicone rubber. $\text{H}_2\text{O}$ and $\text{H}_2\text{S}$ molecules in the air can pass through these pores and enter the inner part of silicone rubber.

In addition, experiments showed that if $\text{NO}_2$, $\text{O}_2$ and $\text{H}_2\text{O}$ are involved in the reaction, the reaction rate will be increased by 1 to 6 orders of magnitude [11]. The content of $\text{NO}_2$ and $\text{H}_2\text{O}$ in the air is
much higher than that of H$_2$S, so the corrosion of Ag is carried out at a high reaction rate. The diffusion model is shown in Fig. 7. It can be seen that, due to the concentration difference between the electrode surface and the air, the diffusion will make the H$_2$S in the air continuously enter the inner part of silicone rubber, leading to the continuous corrosion reaction.

![Figure 7. The diffusion model.](image)

5. **Cause analysis of serious corrosion of this batch of circuit boards**

Different from other batches of circuit boards, the silver electrode corrosion of this batch of circuit boards was particularly serious. The specific surface area and pore size distribution of different batches of silicone rubber (No. I, II, III, among which III is the batch with serious corrosion) were tested by BET. The test results are shown in Table 5. The pore volume and pore size distribution of three different batches calculated by BJH method are shown in Table 6.

### Table 5. Results of the specific surface area and pore size.

| NO. | The specific surface area [m$^2$/g] | Average pore size [nm] |
|-----|-----------------------------------|------------------------|
| I   | 1.1729                            | 2.5                    |
| II  | 0.2122                            | 0.9                    |
| III | /                                 | /                      |

### Table 6. Pore size distribution of different samples.

| Pore Diameter Range [nm] | I     | II     | III    |
|--------------------------|-------|--------|--------|
| Pore Diameter Range [nm] | 411-64| 64-36  | 36-25  |
| Pore Volume [cm$^3$/g]   | 0.000282 | 0.000140 | 0.000030 |
| Percentage [%]           | 55.0 | 27.3 | 5.85 |
| Pore Diameter Range [nm] | 25-19 | 19-15 | 25-2  |
| Pore Volume [cm$^3$/g]   | 0.000029 | 0.000032 | /     |
| Percentage [%]           | 6.24 | /     | /     |

| Pore Diameter Range [nm] | II    | III    |
|--------------------------|-------|--------|
| Pore Diameter Range [nm] | 404-190 | 190-98 |
| Pore Volume [cm$^3$/g]   | 0.000089 | 0.000031 |
| Percentage [%]           | 52.7 | 18.3 |
| Pore Diameter Range [nm] | 98-79 | 79-64 |
| Pore Volume [cm$^3$/g]   | 0.000028 | /     |
| Percentage [%]           | 16.6 | /     |
| Pore Diameter Range [nm] | 64-36 | 36-13 |
| Pore Volume [cm$^3$/g]   | /     | /     |
| Percentage [%]           | /     | /     |

| Pore Diameter Range [nm] | III   |
|--------------------------|-------|
| Pore Diameter Range [nm] | 404-190 |
| Pore Volume [cm$^3$/g]   | 0.000491 |
| Percentage [%]           | 29.4  |
| Pore Diameter Range [nm] | 190-98 |
| Pore Volume [cm$^3$/g]   | 0.000454 |
| Percentage [%]           | 27.2  |
| Pore Diameter Range [nm] | 98-79 |
| Pore Volume [cm$^3$/g]   | 0.000118 |
| Percentage [%]           | 7.07  |
| Pore Diameter Range [nm] | 79-64 |
| Pore Volume [cm$^3$/g]   | 0.000072 |
| Percentage [%]           | 4.32  |
| Pore Diameter Range [nm] | 64-36 |
| Pore Volume [cm$^3$/g]   | 0.000199 |
| Percentage [%]           | 11.9  |
| Pore Diameter Range [nm] | 36-13 |
| Pore Volume [cm$^3$/g]   | 0.000206 |
| Percentage [%]           | 12.36 |

It can be seen from table 5 that the pore of sample III sample is too small to be measured by the instrument. The smaller the pore size is, that is, the specific surface area of silicone rubber is higher, which can absorb more H$_2$S molecules. It can be seen from Table 6 that the pore size distribution of sample III is wide, and the difference of pore size is large. This special pore size distribution will be
more conducive to reduce the diffusion resistance of H₂S molecules in rubber. Therefore, the change of inner hole size of silicone rubber will increase the amount of H₂S, O₂, H₂O passing through the rubber and cause more serious corrosion.

The above analysis results also provide ideas and direction for the improvement of silicone rubber. Through investigation, it was found that the change of viscosity of rubber solution or composition of silica gel would cause the change of hole size inside the rubber[12]. So the main indexes that affect the filling effect of silicone rubber on circuit board are viscosity and surface dry time of rubber. Subsequently, the viscosity index of different batches of glue solution can be tested to determine the viscosity control range and find out the most suitable fluidity to ensure the filling effect.

6. Conclusions
(1) According to the failure analysis of silver electrode and environmental simulation test, it can be seen that the H₂S in the air enters the silver electrode surface through the rubber through the adsorption and permeation effects, and corrodes the silver electrode.
(2) The change of pore size in silicone rubber will affect the H₂S corrosion reaction. The smaller the pore, the higher the specific surface area and the more polar H₂S molecules adsorbed by rubber. The special pore distribution of the size of the intercalation is beneficial to reduce the diffusion resistance of H₂S molecules in rubber.
(3) By controlling the viscosity, composition and surface dry time of the glue solution, the corrosion of H₂S in the air to the silver electrode can be effectively prevent.

7. References
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