# Study on Effect of Silver Migration in Corrosive Environments

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**Abstract**

**Electrochemical Migration (ECM) is a phenomenon that affects the reliability of electrical components like semiconductor devices. Silver, which is known to be particularly susceptible to ECM growth, is used in some semiconductor devices. Our products may unintentionally be exposed to corrosive gases such as low concentrations of hydrogen sulfide at an installation site. Regular in-house evaluation tests are performed in a test environment that assumes a general atmosphere and does not include corrosive gases. For this reason, the effect of hydrogen sulfide on silver ECM is not taken into consideration.**

**We verified the effect of hydrogen sulfide on the growth of silver ECM. In this verification program, the higher the hydrogen sulfide concentration, the more the growth of silver ECM is inhibited. We will draw on the knowledge gained through this experiment for product development to provide highly reliable products.**

## 1 Preface

One of the phenomena that affects the reliability of electrical components such as semiconductor devices is Electrochemical Migration (ECM). Silver is generally a metal that is prone to ECM. In some semiconductor devices, silver is used for plating the terminals.

We deliver power products and electronic devices to a wide variety of customers. The installation environments of our products are diverse and they may unintentionally be exposed to small amounts of hydrogen sulfide. In a corrosive gas environment such as hydrogen sulfide, it is thought that the behavior will be different from that of general ECM tests. In this paper, we focus on hydrogen sulfide as an environmental factor and verify the effect on silver ECM under multiple concentration conditions and provide an overview of the results.

## 2 Evaluation of Silver ECM in Hydrogen Sulfide Environment

Fig. 1 shows an outline of this test. To investigate the effect of hydrogen sulfide on silver ECM, the formation process of silver ECM in air and hydrogen sulfide environments was compared and evaluated. In this test, pure water was dropped between the electrodes on a mock substrate and then an electric current was applied to induce the formation of silver ECM.

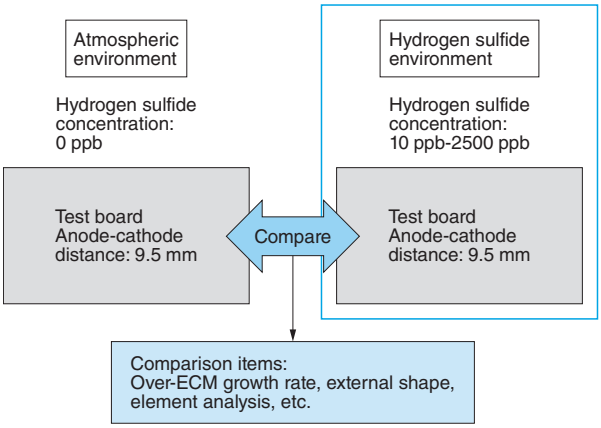



**Fig. 1** Outline of Silver ECM Evaluation Test under Hydrogen Sulfide Environment

Based on a parameter of hydrogen sulfide concentration, the effect of hydrogen sulfide on silver ECM formation is investigated.

### 2.1 Silver ECM Test Method

The silver ECM formation test was carried out using a mock board with silver plating on copper electrodes. After dropping pure water between the

**Fig. 2** Gas Corrosion Test Equipment

Gas corrosion testing equipment was employed for the structuring of hydrogen sulfide environment. With this equipment, high-temperature and high-humidity test can be carried out up to the highest temperature of 85℃ under the atmosphere of corrosive gases.

**Table 1** Test Conditions

For the environment of hydrogen sulfide, a temperature of 40℃ and humidity of 80% were fixed inside the testing tank, and the hydrogen sulfide gas concentration conditions were set at 6 for parameters.

| Testing conditions | Temperature (℃) | Relative humidity (%) | Hydrogen sulfide concentration (ppb) |
|---|---|---|---|
| ① | 40 | 80 | 0 |
| ② | 40 | 80 | 10 |
| ③ | 40 | 80 | 50 |
| ④ | 40 | 80 | 100 |
| ⑤ | 40 | 80 | 800 |
| ⑥ | 40 | 80 | 2500 |

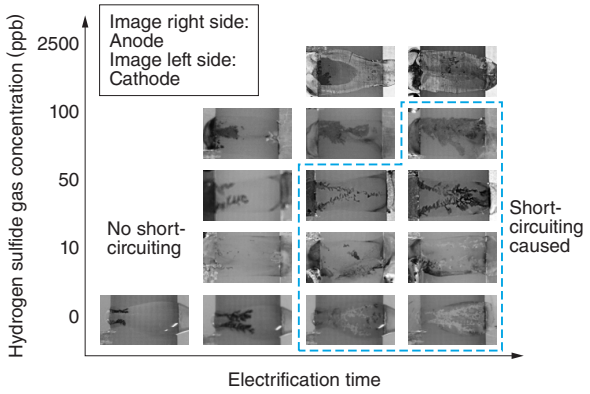



**Fig. 3** Results of Time-Serial Behavior Observation of Silver ECM Formation for Respective Hydrogen Sulfide Concentrations

A tendency was observed such that the ECM growth rate was lowered as the hydrogen sulfide concentration was raised.

electrodes at 9.5 mm on the board, a constant voltage was applied between the electrodes to observe the formation of silver ECM.

The presence or absence of a short circuit due to silver ECM was determined by observing the shape and measuring the interelectrode resistance. In addition, the composition of the formation, such as silver ECM, was evaluated by an Electron Probe Micro Analyzer (EPMA) and an X-ray Photoelectron Spectroscopy (XPS).

### 2.2 Creation of Hydrogen Sulfide Environment

Fig. 2 shows the external appearance of the gas corrosion test equipment called “GS-UVS” by Suga Test Instruments Co., Ltd. A hydrogen sulfide environment was created using this equipment. For the silver ECM formation test, the gas corrosion test device was set to a temperature of 40℃ and a humidity of 80%. The hydrogen sulfide concentration was used as a factor, and the test was carried out under all six conditions shown in Table 1.

## 3 Test Results

Fig. 3 shows the results of the observations over time, from the start of current flow to the formation of silver ECM by concentration condition. Fig. 4 shows the change in interelectrode resistance over time in the same test. The formation of silver ECM spreads in a dendritic shape from the cathode side in all concentrations. In addition, a tendency for the formation rate to decrease with increasing hydrogen sulfide concentration was confirmed. In the test with a hydrogen sulfide gas concentration of 2500 ppb, the formation of silver ECM was suppressed. The formation of a white membrane was also confirmed from the anode side.

Fig. 5 shows the results of mapping analysis of the constituent elements of this white membrane for silver and sulfur by EPMA. The white membrane is clearly a formation in which silver and sulfur are

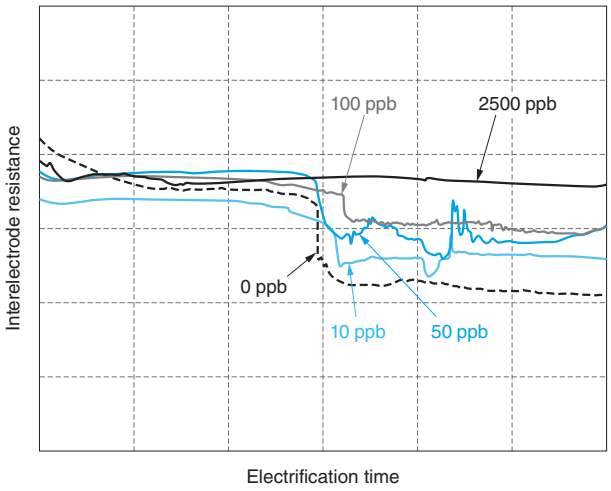



**Fig. 4** Change in Interelectrode Resistance Over Time for Respective Hydrogen Sulfide Concentration Values

The short-circuiting time tends to increase as the hydrogen sulfide concentration rises. Around a high concentration level of 2500 ppb, no short-circuiting seems to occur.

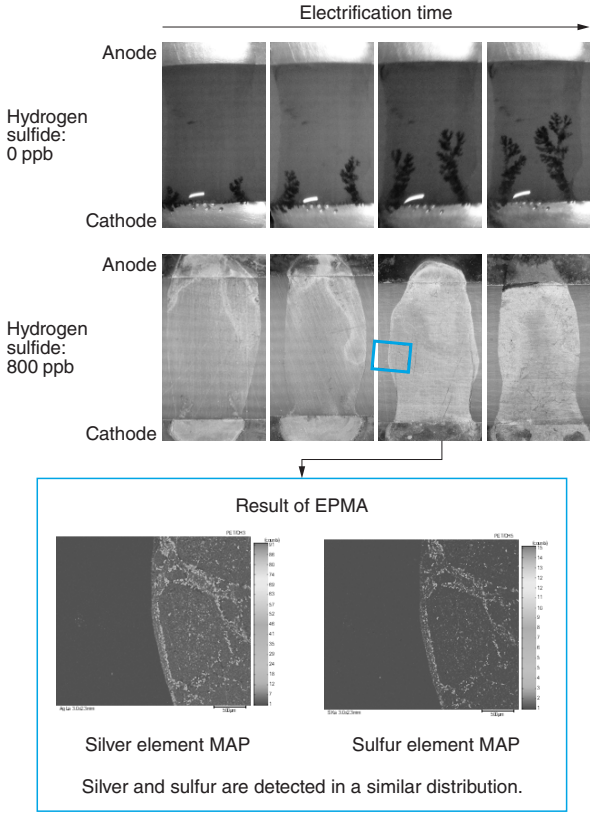



**Fig. 5** Formation of White Membrane in High Concentration Domain and Result of EPMA Analysis

In a domain of high-concentration hydrogen sulfide, the formation of a white membrane around the anode is predominant. The result of EPMA analysis suggests that the white membrane consists of a sulfide of silver (Ag).

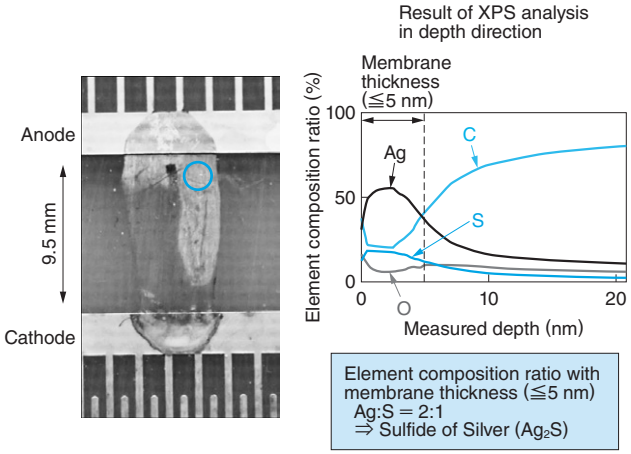
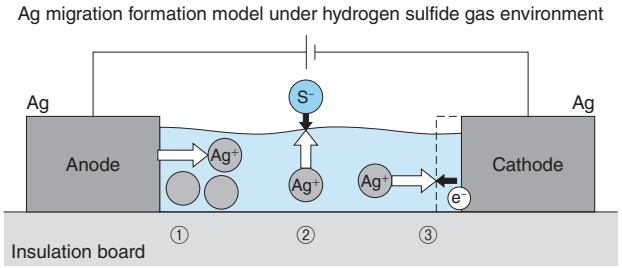



**Fig. 6** Results of White Membrane XPS Analysis in Direction of Depth

According to the transition data of element composition ratio acquired from XPS analysis in the depth direction, it is surmised that the white membrane is silver sulfide with a membrane thickness of approximately 5 nm.




①Ag ionization at anode ($Ag \rightarrow Ag^+ + e^-$)
Applied voltage, dependent on anode surface condition.

②Ag ion trapping on water surface ($2Ag^+ + S^- = Ag_2S$)
⇒ Interference reaction
Dependent on hydrogen sulfide gas concentration.

③Emission of Ag ions from cathode
Remaining ions of ①-② are precipitated.

**Fig. 7** Formation Model of Silver ECM under Hydrogen Sulfide Environment

Regarding the formation of Ag ECM, examination and modeling were implemented on the assumption that hydrogen sulfide is a factor of interference.

distributed similarly. This is presumed to be a silver sulfide-based formation.

**Fig. 6** shows the results of the analysis of the element composition ratio in the depth direction using XPS. From the composition ratio of each element with respect to the measured depth, it is presumed that the membrane thickness is approximately 5 nm. Based on the ratio of silver and sulfur content, it was determined that this membrane was precipitated as silver sulfide.

**Fig. 7** shows a model for the formation of silver ECM in a hydrogen sulfide environment, which was considered based on the results of this test. In gen-

eral, the silver ECM reaction proceeds by silver ions eluted from the anode being precipitated at the cathode via the water component between the positive and negative electrodes on the substrate surface. The results of this test revealed, however, that silver sulfide was precipitated. In a hydrogen sulfide environment, hydrogen sulfide reacted with the water component from which silver ions were eluted. As a result, the relative number of silver ions that reached the cathode and precipitated as silver ECM decreased. In other words, it is considered that hydrogen sulfide acted in an inhibitory direction on silver ECM.

## 4 Postscript

In this study, we verified the effect of hydrogen sulfide concentration, one of the environmental factors, on silver ECM. We confirmed that hydrogen sulfide concentration does not accelerate silver ECM under simulated conditions. We will carefully examine whether there are any combined effects with other environmental factors and will use these results to improve reliability evaluation technology in the future. We will also utilize the knowledge obtained from the analysis of chemical species that are produced by a chemical reaction. It can be useful for identifying the cause of failures due to corrosive environments and proposing improvements to the product installation environment. Through these efforts, we intend to contribute to the development of highly reliable products and the reduction of product failure risks.

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