Electrochemical migration of Ag in Na_2SO_4 environment

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***Abstract*— The effect of sulphate ion concentration on electrochemical migration (ECM) of silver was investigated by applying an in-situ optical and electrical inspection system. It was found that dendrites grow not only in an electrolyte solution with low sulphate ion concentration but also in electrolytes with medium and high or even saturated sulphate ion concentrations. According to the Mean-Time-To-Failure (MTTF) values, the migration susceptibility was decreased with the increase of sulphate ion concentration in case of low and medium concentration levels. However, the ECM susceptibility was increased at saturated concentration level.**

Keywords*— *electrochemical migration; water drop test; Na_2SO_4 solution; Ag.

I. INTRODUCTION

Many reliability issues of electronics have to be solved nowadays [1-3]. One of the most dangerous ones is the electrochemical migration (ECM) failure phenomenon.

ECM may pose a high reliability risk related to electronics applications [4]. The ECM failure phenomenon occurs in the presence of moisture in the case of operating circuits: the dissolution of metals starts at the anode and produces metal ions, which are driven by the applied electric field and migrate to the cathode, where they can deposit as pure metals – dendrites (See Fig. 1). Dendrite formation can lead to a short. Many types of the metals widely used in the electronics industry have relevant susceptibility for ECM, such as Sn, Ag or Cu [5]. Silver is also widely investigated related to ECM [5-10].

Usually, ECM tests were carried out by three main methods; water drop (WD) test [11], environmental tests under different thermal-humidity conditions [12] and by various electroanalytical methods, like voltammetry or polarization tests [13]. The electrochemical corrosion and ECM tests of Ag were usually carried out in a bulk solution. On the other hand, the importance of thin electrolyte layers (TEL) is growing, since ECM ability depends on the thickness of water layer as well [14]. Furthermore, the concentrations of the applied electrolytes had a wide variety as well: deionized water [5], acidic or alkaline solutions [15] and also salt solutions [16], which usually simulate the possible contamination effects. In the electronics industry, one of the common contaminants is the sulphate ion, which can strongly modify the electrochemical corrosion processes and thus, the migration behavior of silver as well. Silver ions can combine with OH^- groups and also with SO_4^{2-} ions and form complexes in a sulphate aqueous solution [17]. The influence of SO_4^{2-} on silver ECM behavior was already investigated in low concentration (0.1 mM Na_2SO_4) at bulk solution [17].

Although the impact of Na_2SO_4 on ECM was already investigated in low concentration, the effect of other concentrations of sulphate ion was not reported related to the ECM of silver. Therefore, the migration behavior of silver effected by sulphate ion is not well understood. On the other hand, simulating the effect of sulphate ion contamination on ECM is an important factor, since sulphate ions can result from the different technological steps during production processes. So, in this study, different concentrations of Na_2SO_4 solution were applied in order to investigate the impact of sulphate ion concentration on ECM in terms of immersion silver as a widely used surface finish in electronics.

Fig. 1. Scanning electron microscope (SEM) image of dendrites.

II. EXPERIMENTAL

In order to simulate the effect of sulphate ion on ECM in the case of silver, a pure copper layer was coated with immersion silver (iAg), which surface finish is applied in the conventional Printed Circuit Board (PCB) technology. The dimensions of the iAg patterns were 2×5 mm, which structure was prepared on a widely used FR4 substrate. The gap size between the electrodes on the test board was 0.5 mm (See Fig. 2).

The whole measuring platform can be seen in Fig. 3. The platform can follow the different ECM mechanisms by optical means and by real-time voltage measurements as well. Simultaneously, the ECM mechanisms were in-situ observed by using a USB microscope (type: XCAM MAN1001-SA) for visual inspection and real-time voltage measurement (Novus Automation MyPCLab 6014) was also applied to better understand (verify) the optical results. The real-time voltage measurement is very characteristic for the dendrite growth (Since the dendrite grows as a function of time, the voltage increases also as a function of time, simultaneously). The voltage was measured on a serially connected 10 MΩ resistor, which is located on the negative pole of the test board (See Fig. 3.), while the optical part provides qualitative information, for example about the dendrite structures, growing directions, different residue formations, (out)gassing, etc.

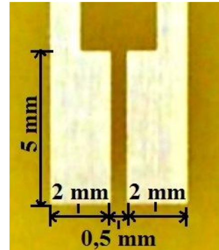

Fig. 2. Immersion Silver test board for ECM test.

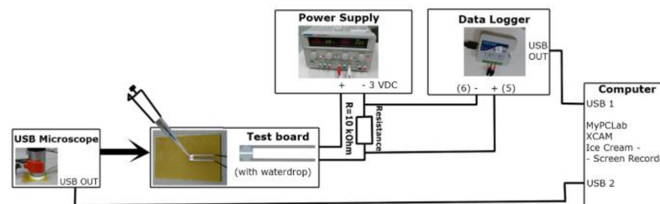

Fig. 3. Schematic of the measuring platform for ECM investigation.

Before each water drop (WD) test, the iAg electrodes (test boards) were rinsed with distilled water, degreased with acetone, and dried in cool air. The electrolyte was Na_2SO_4 solution of various concentrations (0.1mM, 1mM, 10mM, 500mM and saturated), which was prepared from deionized water (18.2 MΩ*cm in resistivity) and from analytical grade reagents. The droplets (volume: 15 µl) were placed by a micropipette onto and between the iAg electrode surfaces. A DC bias of 3V was applied between the two electrodes. To check reproducibility, all the WD tests were repeated for at least eight times. The Mean-Time-To-Failure (MTTF) was also calculated from the real-time voltage measurements, where the failure criterion was the first voltage jump (see Fig 4.).

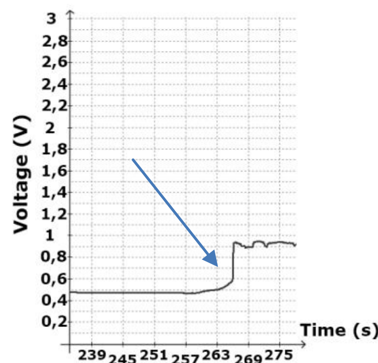

Fig. 4. Voltage jump as a failure criterion for MTTF calculation.

III. Results and Discussion

A. ECM of iAg in 0.1 mM Na_2SO_4 solution

In this case, only dendrite formation occurred during the WD test. However, the dendrite formation was very rapid, MTTF was about 9 sec. A typical optical result can be seen in Fig. 5.

Fig. 5. Only dendrites formed in 0.1 mM Na_2SO_4 solution during WD test.

B. ECM of iAg in 1 mM Na_2SO_4 solution

At this concentration level, an intensive (H_2) gassing occurred at the cathode first, and afterwards a blue colored residue formed (see Fig. 6). Four or five minutes later, the first dendrite occurred. In this case, the MTTF value was about 6 minutes.

Fig. 6. Dendrite and blue/dark blue colored residues formed in 1 mM Na_2SO_4 solution during WD test.

The significantly increased MTTF can be explained by the formation of the blue colored residue, since the residue can hinder or even stop the migration of the metal ions. The residue indicates that the solubility of the solution has dramatically changed (lower solubility). Therefore, the possible concentration of the silver ions also decreased. So, depending on the residue type, different solubility products show up in the solution, which can significantly modify the possible metal ion concentration and can therefore have significant effect on MTTF as well.

C. ECM of iAg in 10 mM Na_2SO_4 solution

With the further increase of the Na_2SO_4 concentration level, the first 6-7 minutes belonged to the intensive H_2 gassing on the cathode, while different colored (white-blue, black) residues formed in the middle of the electrodes, which moved to the anode side (See Fig. 7.). The MTTF value significantly increased up to 16.5 minutes.

Fig. 7. Different type of residues (white-blue, black) and dendrites formed in 10 mM Na_2SO_4 solution during WD test.

D. ECM of iAg in 500 mM Na_2SO_4 solution

In this case, a continuous gas evolution was observed on the cathode, while different colored (blue, black, dark brown) residues formed (See Fig. 8.) between the anode and the cathode. According to the voltage measurements, dendrite formation also occurred, and after 25 minutes, a salt crystal formation started. The crystallization started on the border line of the droplet and the dendrites grew under the salt crystals. The MTTF value was about 34 minutes.

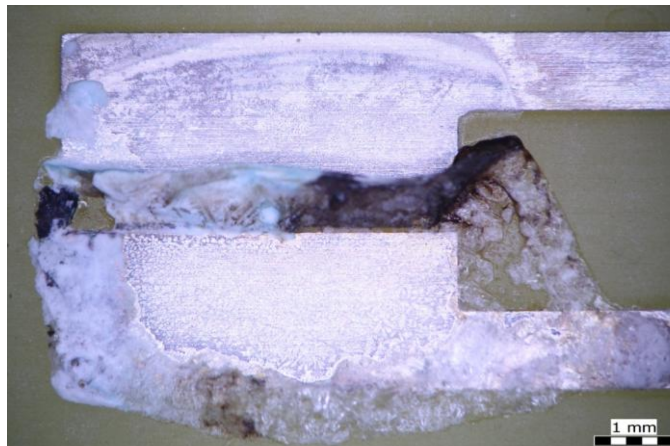

Fig. 8. Different types of residues (blue, black, dark brown) and dendrites under the salt crystals were formed in 500 mM Na_2SO_4 solution during WD test.

E. ECM of iAg in saturated Na_2SO_4 solution

In the first period of the WD tests, intensive gassing started on the cathode as usual, while salt crystal formation occurred on the anode along the border of the droplet. Between the conductors, white-blue residues were formed. These residues grew towards the cathode as well as to the anode side. After the residues were reached both of the electrodes, the gassing intensity were decreased and the salt content of the droplet started to form crystals. The first dendrite appearance occurred after about 19 minutes. In Fig. 9., the formed salt crystals and white-blue residues can be seen. In this case, the MTTF was about 23 minutes.

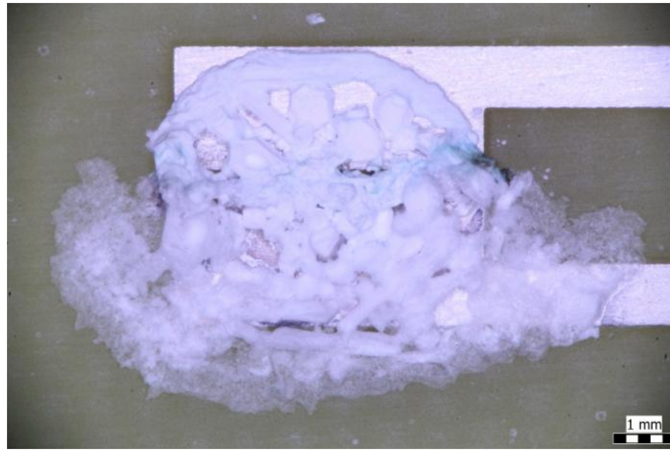

Fig. 9. Blue colored residues and dendrites under the salt crystals formed in saturated Na_2SO_4 solution during WD test.

It can be seen in Fig. 10 that an increasing tendency of MTTF was observed up to 500 mM of Na_2SO_4. However, the saturated case showed a relatively low MTTF value, which is an unexpected result. As it was already mentioned, on the one hand, MTTF depends on the types (and sizes) of the residues formed. In this respect, the different residues have different solubility product constants, and therefore different concentrations of metal ions can exist, which have a huge influence on the ECM probability. On the other hand, the Na_2SO_4 concentration level has an impact on the change of the pH value as well. Furthermore, the probability of metal ion formation (active, passive or immunity region) depends also on the pH values in the aqueous solution, which was first reported by Pourbaix [18].

It can be also seen (Fig. 6-9.) that the higher concentration level produces even larger and larger residues during the WD tests. So, the concentration level may have an influence on the residue size as well.

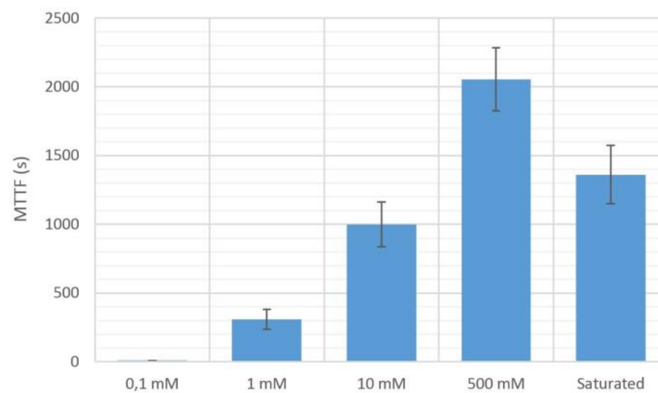

Fig. 10. Summary of the MTTF values in case of different concentration levels after WD tests on iAg surface finishes.

IV. Conclusions

The effect of sulphate ion concentration on ECM of iAg was investigated by applying an in-situ optical and electrical inspection system under various Na_2SO_4 concentrations: 0.1 mM; 1 mM; 10 mM; 500 mM and saturated solution.

In the case of 0.1 mM Na_2SO_4 solution, no residue formation was detected due to the very low concentration level. So, the residues do not take part in the ECM mechanism and therefore the short formation mechanism is the fastest.

In the case of 1 mM, 10 mM and 500 mM Na_2SO_4 solutions, different and even larger and larger residues were formed, respectively. The concentration level may have an influence on the residue size, and the residue type and size may have an influence on the MTTF as well.

However, in the case of the saturated solution, a relatively lower MTTF was observed. This can be explained by the similar residue type (mainly white-blue) compared to the 10 mM ones and by the very different residue types and sizes compared to the 1 mM and 500 mM ones.

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