

Electrochemical Migration of Cu and Sn in Na₂SO₄ Environment

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Abstract: *The effect of Na₂SO₄ concentration on electrochemical migration (ECM) of copper and tin was investigated applying an in-situ optical and real-time electrical inspection system. According to the Mean-Time-To-Failure (MTTF) values, the ECM susceptibility of copper has increased at low concentration levels. However, the ECM susceptibility of copper has decreased at the medium and stopped at the high and even saturated concentration levels. On the other hand, the ECM susceptibility of tin has increased at low levels. Afterwards the ECM ability of tin was hindered and even stopped at medium level. Interestingly, the ECM susceptibility of tin was reappeared at high concentration levels.*

1. INTRODUCTION

Electrochemical migration (ECM) is a kind of humidity induced failure, which can lead to high reliability risk from the operating electronics point of view [1]. According to the classical model of ECM, the failure mechanism starts on the anode with the dissolution of metals and forms metal ions. The directions of the metal ion migration are dominated by the applied voltage (electric field) towards to the cathode, where they can deposit as pure metals and resulted in dendrites (See Fig 1). So, the dendrites are kinds of conductive filaments and therefore, they can form shorts. Many types of metals that are widely used in the electronics have relevant ability for ECM, such as tin, silver or copper [2]. Next to Ag, Cu and Sn are also widely studied from the ECM point of view [2-10].

Usually, ECM investigations are carried out by the following methods; water drop (WD) tests [11], environmental tests using climatic chambers [12] and by various electroanalytical technics, such as cyclic voltammetry [13] or electrochemical impedance spectroscopy [14]. The electrochemical corrosion and ECM tests of Cu and Sn were usually investigated in bulk solutions [2, 4, 6, 10, 15]. On the other hand, the importance of thin electrolyte layer (TEL) tests are growing [16, 17], hence ECM susceptibility depends also on the thickness of water layer [18]. Furthermore, the types of the applied electrolytes had a wide variety as well: high purity water [2], acidic or alkaline electrolytes [19] and also salt solutions [20], which simulate the different contamination effects.

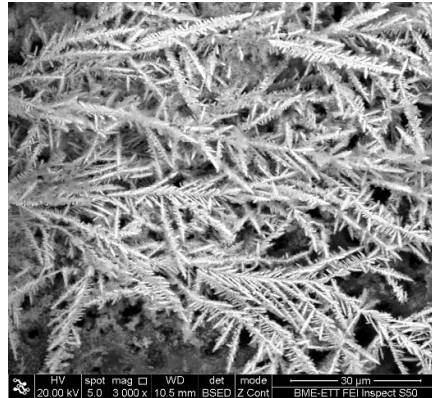


Fig.1. Dendrites caused by ECM.

Among the applied technological processes of electronics and used materials a common contaminant is the sulphate ion, which has an effect on the electrochemical corrosion processes and thus, also on the migration behavior of copper and tin. Copper and tin ions can combine with $[\text{OH}]^-$ groups and also with $[\text{SO}_4]^{2-}$ and form complexes in sulphate contained aqueous solutions [2, 7, 21, 22]. On the other hand, the influence of $[\text{SO}_4]^{2-}$ on copper and on tin ECM is not deeply addressed in the literature. Furthermore, simulating the effect of sulphate ion contamination on ECM is an important factor, hence sulphate ions can be found in the different technological processes. In this study, different concentrations of Na_2SO_4 solution were investigated in order to find out the effect of sulphate ion concentration on ECM in terms of copper and tin.

2. EXPERIMENTAL

Pure copper and electroplated tin on copper with the dimensions of $2 \text{ mm} \times 5 \text{ mm}$ were prepared on an FR4 substrate using conventional printed wiring board technology. The gap size between the conductor traces on the test board was 0.5 mm (See Fig. 2).

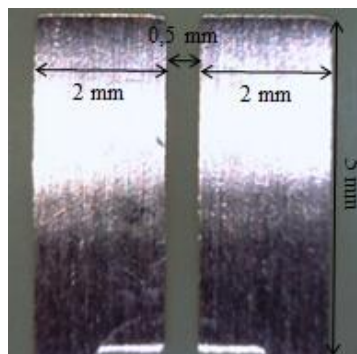


Fig. 2. Prepared sample used in WD tests.

The platform (See Fig. 3) can follow the different ECM processes with visual (in-situ) and also with a real-time voltage measurement. The real-time voltage measurement is characteristic for the dendrite growth (sort formation).

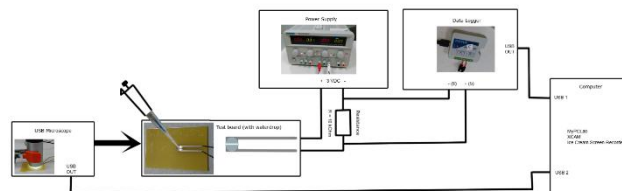


Fig. 3. Schematic of the measuring platform for ECM investigation.

Before each experiment, the sample surfaces were rinsed with deionized (DI) water, degreased with isopropyl alcohol subsequently, and dried in cool air. The electrolyte was Na_2SO_4 bulk solution with various concentrations (0.1mM, 1mM, 10mM, 500mM and saturated), which was prepared from DI water (18.2 M Ω cm in resistivity) and from analytical grade reagents. As a reference the ECM susceptibility of Cu and Sn was also measured in DI water as well. In each experiment 10 μl droplet was placed onto the traces of the sample (see Fig. 2) using a micropipette. The test voltage was 3 VDC in all cases. Simultaneously, the different electrochemical processes were in situ observed using a USB microscope. To check the reproducibility, all the ECM tests were repeated at least ten times. The Mean-Time-To-Failure (MTTF) and deviations were also calculated from the real-time voltage measurements, where the failure criterion was the first voltage jump (See Fig. 4).

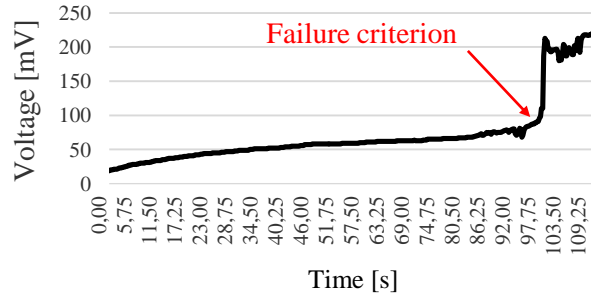


Fig. 4. Example for MTTF calculation.

3. RESULTS AND DISCUSSION

3.1 ECM results of Cu in Na_2SO_4

During the first experiments, deionized water was used as reference. In this case only dendrites were grown (See Fig. 5) and the MTTF was about 149 sec.

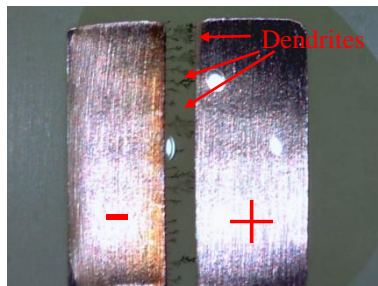


Fig. 5. Cu dendrites were formed during the WD test using DI water.

In case of 0.1 mM Na_2SO_4 the only difference was that the failure process (dendrite growth) was faster (MTTF = 68.5 sec). In case of 1mM Na_2SO_4 the MTTF was about 61 sec. Furthermore, next to the dendrite growth, H_2 outgassing (Fig. 6) and a small amount of residue were also detected (See Fig. 7). After increasing the concentration up to 10 mM Na_2SO_4 , significant changes occurred. Namely, the MTTF was increased up to 472 sec, while the outgassing was more intense (See Fig. 8) and a huge volume of residue (Fig. 9) was also formed. This trend was continued at 500 mM and even at saturated levels. That means the migration process was stopped at high concentration levels, hence no dendrites were detected. On the other hand, the gassing mechanism was extremely intensive next to huge volume of residue formations (Fig. 10).

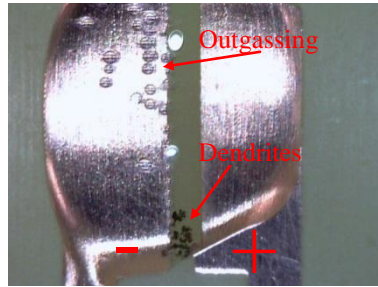


Fig. 6. H₂ gas evolution and dendrites were formed during WD test using 1 mM Na₂SO₄.

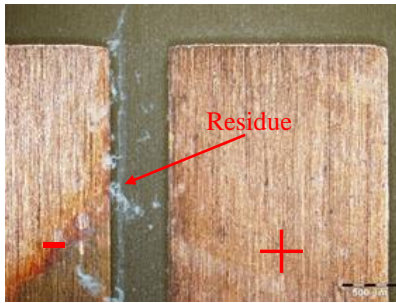


Fig. 7. Pale blue residue was formed during WD test using 1 mM Na₂SO₄.

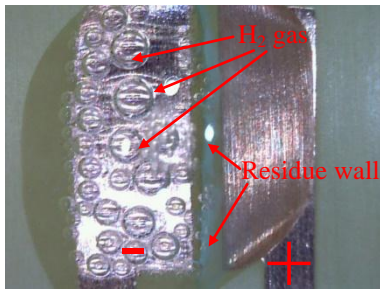


Fig. 8. Pale blue residue “wall” was formed during WD test using 10 mM Na₂SO₄.

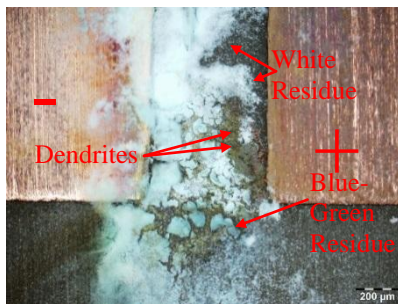


Fig. 9. White and blue-green residues were formed during WD test using 10 mM Na₂SO₄.

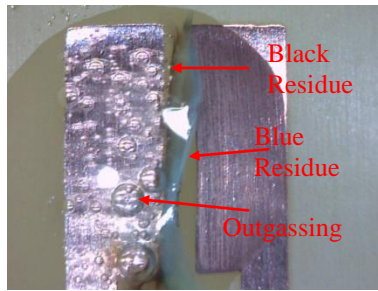


Fig. 10. Black and dark blue residues were formed during WD test using 500 mM and saturated Na_2SO_4 .

The summary of MTTF values of copper ECM can be seen in Fig. 11. According to the Mean-Time-To-Failure (MTTF) values, the velocity of dendrite growth has increased at 0.1mM and 1 mM Na_2SO_4 compared to the case of deionized water. However, the velocity of dendrite growth has decreased at the 10mM and stopped (MTTF = 0 sec) at the 500 mM and even saturated concentration levels. This phenomena is caused by the formed residues with all likelihood.

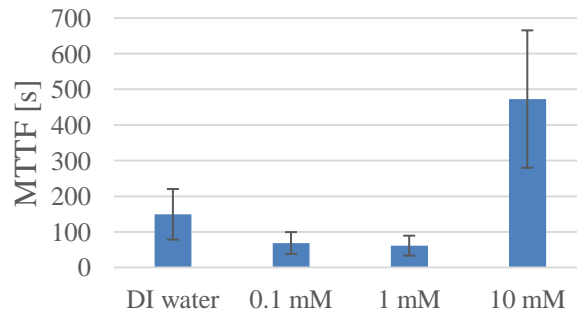


Fig. 11. MTTF and deviations (1σ) after WD test of Cu using different Na_2SO_4 concentrations.

3.2 ECM results of Sn in Na_2SO_4

During the first experiments deionized water was used as reference. In this case only dendrites were grown (See Fig. 12) and the MTTF was about 166 sec.



Fig.12. Dendrites were formed during the WD test using DI water.

In case of 0.1 mM Na_2SO_4 the only difference was that the failure process (dendrite growth) was faster (MTTF = 83 sec) and some H_2 gas evolution was detected. However, in the case of 1 mM Na_2SO_4 , the ECM ability was significantly decreased (MTTF = 582 sec) and next to the more intense gas evolution some residue was occurred as well (Fig. 13).

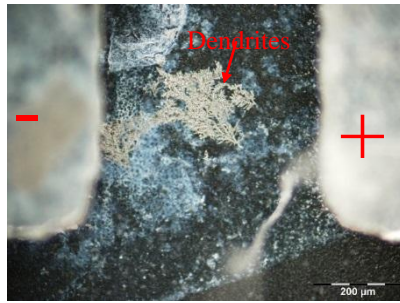


Fig. 13. Dark blue residue and dendrites were formed during WD test using 1 mM Na_2SO_4 .

In the case of 10 mM Na_2SO_4 , no dendrites were detected (MTTF = 0 sec), while a relative huge volume of residue was formed (Fig. 14).

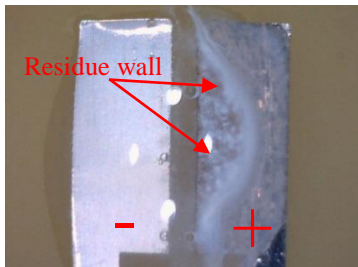


Fig. 14. Blue residue wall was formed during WD test using 10 mM Na_2SO_4 .

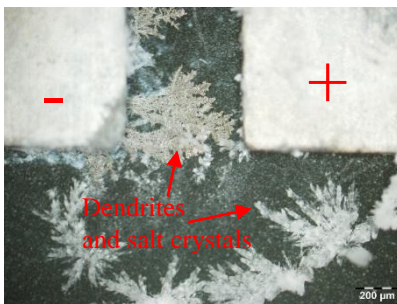


Fig. 15. Salt crystals and dendrites were formed during WD test using 500 mM and saturated Na_2SO_4 .

Interestingly, the ECM susceptibility of tin was reappeared at 500 mM concentration and even at saturated levels. In both cases salt crystals and dendrites (Fig. 15.) were remained after WD test.

The main difference between the two cases was the ECM susceptibility. The MTTF value in the 500 mM case was about 231 sec, while in the saturated solution the MTTF was 467 sec. The summary of the MTTF values can be seen in Fig. 16.

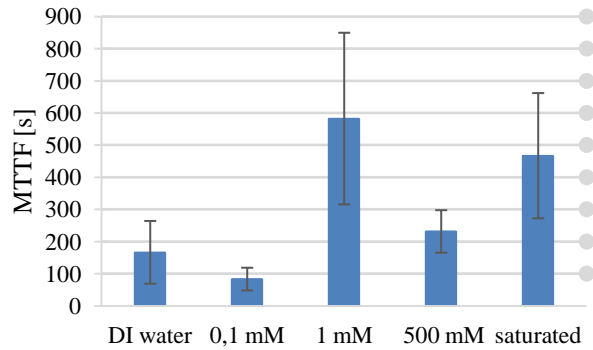


Fig. 16. MTTF values and deviations (1σ) after WD test of Sn using different Na₂SO₄ concentrations.

According to the Mean-Time-To-Failure (MTTF) values, the velocity of dendrite growth has increased at 0.1mM Na₂SO₄ compared to the case of the deionized water. However, the velocity of dendrite growth has decreased at the 1 mM and stopped at the 10 mM concentration level (MTTF = 0 sec). This phenomena is caused by the formed residue wall with all likelihood. However, the ECM ability was reappeared at 500 mM and at saturated concentration levels, which is an unexpected result. In order to explain unexpected result, further investigation are needed to identify for example the elemental composition and/or the chemical state of the formed residues caused the different electrochemical processes.

4. CONCLUSIONS

The effect of Na₂SO₄ concentration on electrochemical migration of copper and tin was investigated applying an in-situ optical and real-time electrical inspection system. Mainly the dendrite and residue formations were observed visually using water drop test. On the other hand, the short formation mechanism was measured by electrically to calculate the Mean-Time-To-Failure (MTTF) data. According to the MTTF values, the ECM susceptibility of copper has increased at low concentration levels (0.1 mM and 1 mM). However, the ECM susceptibility of copper has decreased at 10 mM and stopped at 500 mM and even saturated concentration levels. On the other hand, the ECM susceptibility of tin has increased at 1 mM concentration. Afterwards the ECM ability of tin was hindered and even stopped at medium level (10 mM). Interestingly, the ECM susceptibility of tin was reappeared at high concentration levels (500 mM and saturated), which was an unexpected result. Further investigations are needed to explain this result.

ACKNOWLEDGEMENTS

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