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Budapest University of Technology and Economics
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INVESTIGATION OF ELECTROCHEMICAL MIGRATION IN MICROELECTRONICS

PHD THESIS

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Introduction

My research field is focused on the electrochemical migration (ECM) phenomenon, with the general aim to improve the reliability of electronics. The common characteristics of the ECM phenomenon include the presence of moisture on conductor-dielectric-conductor systems under bias voltage, the electrochemical process and the metallic dendrite growth. This process is driven by an applied electric field from the anode to the cathode. Dendrite growth occurs as a result of metal ions being dissolved into a solution. These escape from the anode and are deposited at the cathode, growing in needle- or tree-like formations. This effect causes short-circuits in the electronic circuits, which may lead to a catastrophic failure.

Due to the growing demands in the electronics industry for miniaturization and increased integration and thus the growing density of conductive layers and the decreasing distances between the leads of electronic components, smaller and smaller areas have to be investigated by using interdisciplinary knowledge. For this reason, our research center is equipped with special equipments which can investigate solid phase conductive, insulating and semiconductor structures and, in some cases, can even carry out liquid-phase measurements between all scales from the human visibility to nano sizes. For these purposes, the department has optical microscopes (Olympus SZX9 and BX51), an X-ray microscope (Dage XiDAT 6600), a scanning electron microscope (FEI Inspect S50) with an energy disperse X-ray spectrometer unit (Bruker Quanta EDX), a scanning acoustic microscope (Sonix HS 1000), X-ray fluorescence spectroscopy (Spectro Midex M), and an atomic force microscopy (Veeco diInnova). In order to perform investigations under harsh environments, different environmental chambers can be applied; a Highly Accelerated Stress Test chamber (Tabai Espec); two Thermal-Humidity Chambers (EHS-211M and Weiss, WK 180/40), and a Thermal Shock Chamber (Tabai Espec, TSE-11-A).

Nowadays, because of the keen competition in the electronic industry, customer requirements must be ranked first. Therefore, it is increasingly important to ensure the reliability and quality of electrical devices by using cost effective technologies. Depending on the applications, the requirements of customers are different, but all of them would like to know whether the lifetime, quality and reliability of the devices will meet their requirements. From the aspect of ECM reliability problems, the main topics are investigations of physical and chemical behaviors on different surface finishes, solder alloys and joints. The Restriction of Hazardous Substances (RoHS) operative directive [1] has just increased the complexity of this challenge as lead bearing solders have to be replaced with lead-free ones. In this context, alternative binary alloys have been examined as replacements for Sn-Pb (traditional) solders, such as near-eutectic Sn-Ag, Sn-Cu, and Sn-Zn alloys. However, ternaries (Sn-Ag-Cu, Sn-Zn-Ag, Sn-Zn-In, etc.) and even quaternary alloys (Sn-Zn-Ag-Al, Sn-Ag-Bi-Cu, Sn-In-Ag-Sb) have also been studied as candidates for lead-free solders. The reliability investigation of lead-free solders is still a very current issue among the researchers, and one of the important topics is electrochemical migration (ECM) failure phenomenon [2, 3].

The first theoretical explanation of the phenomenon was given in connection with the silver migration [4]. In this migration model, dendrites are grown on the cathode by the deposition of anodically dissolved ionic constituents that are present in the conductive strips. The migrated resistive shorts occur at practically random locations, and emerge mainly under extreme conditions (i.e. high temperature and humidity). However, a number of electrical field-governed failure types are correlated with migration. A device can operate for many hundreds of hours under normal operating conditions, and then, after a short exposure to special environmental conditions, it may fail suddenly [4]. Later it was proven in numerous further studies that several other metals also show dendrite growth caused by ECM, i.e. Cu, Pb and Sn. Furthermore, it was also proven that ionic contaminants have a high impact on ECM as well. Nevertheless, the presence of new lead-free based solder materials generated an increasing need to investigate them for the ECM phenomenon. Even recent publications have pointed out the importance of this research field [5, 6].

Motivation

According to the state of the art, the ECM phenomenon has got still many open questions such as undefined reactions and processes. The existing models cannot adequately describe the whole process of ECM. The interpretation will be difficult indeed, due to the novel lead-free solder alloy systems which involve different electrochemical processes. These electrochemical processes occur in very small amounts of electrolytes (~μl), furthermore the processes are not stationary and the systems are not homogeneous as well. Therefore, there are no descriptions of equations, only empirical models exist [7].

Usually, the investigations are carried out in two different scenarios: one of them is done under laboratory circumstances (at room temperature and humidity), while the other one is carried out in extreme climatic conditions. The latter one is carried out by environmental tests, which provide high temperature and humidity levels, while the patterns are followed by some kinds of electrical parameters, such as surface insulation resistance, leakage current or voltage changing. However, the environmental tests provide data mainly about the ECM processes (fault detection) and give very little useful information about the antecedent processes such as water condensation mechanism. Although environmental chambers (tests) can simulate the mechanism of water condensation, there is little information available about the physical aspects of condensation which leads to ECM and dendrite growth [8]. Another open question is the impact of condensation time on the mean time failure time (MTTF); it can be supposed that the time ratio between condensation time and electrochemical migration time (dendrite growth) is not irrelevant in certain cases. There are also many contradictory statements in the literature. A contradictory statement can be found about the comparison of the ECM behavior of copper and lead. Presently, an accepted ranking of the ECM susceptibility of silver, copper, tin and lead is the following: Ag>Pb>Cu>Sn (Silver is the worst). This ranking, which refers to time to failure was correlated with the different solubility product constant of different metal hydroxides (e.g. $Sn(OH)_2$). The recent literature contains very different values about solubility product constants of lead(II)hydroxide. In addition, not pure Pb was used (Pb bearing solder alloy) in the experiments [9]. Finally, many studies were carried about lead-free micro-alloyed low Ag content solders relating different reliability issues, like solderability, intermettalic compound (IMC) evaluation, shear strength behavior, tensile and wettability properties or electromigration behavior which is another phenomenon than ECM. However, ECM investigations of the novel lead-free micro-alloyed low Ag content solders were not found in the literature.

Research goals

1. The first aim of my research was to gain a better understanding of the antecedent processes of ECM short formation. Therefore, the effect of condensation on the total failure mechanism had to be clarified. Thus an improvement of a novel measuring method was aimed, which provides new information about ECM behavior, for example the water condensation process during Thermal-Humidity Bias (THB) tests.

2. The second aim addresses the ECM-related condensation mechanism. Supposedly, the condensation time (MTTC) strongly depends on the capillary effect and on other physical and chemical properties, such as wetting ability and/or water adsorption. In other words, the speed of MTTC could be mainly determined by the type of insulation material, since it can be supposed that in some cases the MTTC time has a close relevance to MTTF. If the hypothesis is proven, then the current migration models [4] have to be modified with the MTTC.

3. Thirdly, there are still many contradictory statements in the literature. One of them is about the ECM susceptibility of Pb and Cu, where a rank of ECM susceptibility was established: Ag>Pb>Cu>Sn (Silver has the highest susceptibility for ECM) [9]. The aim of this investigation is to make easier the material choice for electrical circuit design, fabrication and reliability.

4. Finally, the last aim is focused on the ECM behavior of the novel lead-free micro-alloyed solder materials. It is known that there is a huge difference in ECM behavior between the lead-bearing and lead-free solder alloys [10]. Therefore, comparative investigations of different solder alloys were carried out focusing on ECM. The comparison was based on the investigation of active and passive local cells on solder surface and structural and composition investigations of dendrites.

Methodology

Environmental testing methods like THB test are the main investigating methods; however, the so called water drop (WD) test is also widely used at present. In case of the environmental tests, samples are stored in a climatic chamber where temperature is higher than room temperature and/or relative humidity is also high. This "aging" process is a common procedure in electronics for testing factors which, taken together or separately, influence the development of the reliability issues. However, it is less suitable for qualitative observation since the process is not as fast as the water drop test. Quantitative comparison is possible when the different samples are tested under identical conditions (relative humidity, temperature, voltage) and the changes of electrical parameters are monitored (e.g. insulation resistance or leakage current).

In the WD test, a well-defined liquid drop (volume, concentration) is placed onto a conductive-dielectric-conductive structure, and a few volts (DC) is applied. Meanwhile, the formation of dendrites can be visually observed, the time dependence of the electrical parameter is measured and, finally, an average value is calculated (Mean-Time-To-Dendrite: MTTD). This is a very qualitative method as it does not model real circumstances. The advantage of this method is that the electrochemical migration susceptibility of metals can be easily and quickly established which makes it cost-effective as well.

Apart from environmental tests and WD tests, different surface analysis methods are also required. The surfaces of the samples are observed with scanning electron microscope (SEM). In this case, the aim is the topographical mapping of the surface for which purpose magnifications up to 100,000x can be reached.

The composition of the surface can be determined by element mapping by using the EDS (Energy-dispersive X-ray spectroscopy) method. EDS is a method available for determining the composition of materials at a defined point or area, which can present either atomic or mass ratio.

X-ray Photoelectron Spectroscopy (XPS) is also applicable for ECM investigations.. In this technique, the sample surface is bombarded with a high energy (3–10 kV) primary electron beam, which results in the emission of secondary, backscattered and Auger electrons from the area of bombardment and these can be readily detected and analyzed. The secondary and backscattered electrons are used for imaging purposes similar to scanning electron microscopy (SEM). On the other hand, all elements in the periodic table, except hydrogen and helium, can be detected and their concentration can be determined.

Novel scientific results

I. Thesis

I have introduced a novel in situ and real time monitoring system which is suitable for optical observations and simultaneous electrical parameter measurements during ECM processes inside climatic chambers. The monitoring system provides extended information about the ECM phenomenon, which is useful for a better understanding of the total ECM process. A novel qualitative model was established with the above mentioned monitoring system:

1. **Small droplets of the dew condensation occur on conductor lines (nucleation) and the substrate is probably covered by even smaller droplets (there is no continuous water film).**

2. **The sizes of the water droplets become bigger and the formation of water islands starts on the conductor lines (no continuous water film, no dendrites).**

3. **Start of the water bridging on the insulation gaps between the conductor lines, and start of the dendrite growth (later short failure).**

Discussion: The novel *in situ* and real time monitoring system was verified by electrical parameter measurements and provided a novel qualitative information related to water condensation and the following dendrite formation processes. It was obtained that the more intense water condensation processes started on metal surfaces.

The phenomenon of “*water-bridge*” formation was first obtained and published as a direct indication/starting process of ECM. My results contain further novelty as well, hence the related ECM literature supposed that the water condensation appears first on the substrates and after filling its “pores” up with water (like a sponge) before the start of the dendrite growth [11].

Related Publications: L1, R1

II. Thesis

With the adjustment of the above mentioned *in situ* and real time monitoring system (see Thesis I.), it can be concluded that Mean-Time-To-Condensation (MTTC) has a significant impact on Mean-Time-To-Failure (MTTF) if the only difference is the insulation material (FR4 vs. PI). I have demonstrated that the insulation material has also high impact on the whole failure process, not only the type of metallization. In this context the wetting behaviour and the thermal parameters of the substrate have to be considered as well. Therefore, considering the above mentioned statements, the existing ECM model needs to be extended as follows:

$$\boldsymbol{MTTF = MTTC + MTTD,}$$

where MTTD is the Mean-Time-To-Dendrite formation.

Discussion: The differences of MTTC can be explained by the different *surface roughness*, different *wetting behaviour* and different *thermal diffusivity*[1] parameters of the substrates. The surface roughness was significant higher in case of FR4 (2.56 ±0.5 μm) than in PI (1.69 ±0.3 μm). The different surface roughness effects on the hygroscopic behaviour. The wetting behaviour influences also the formation of continuous water film. Due to exothermic nature of the condensation process, the so called thermal diffusivity must be also into consideration between substrates. The better (bigger) thermal diffusivity (α_{FR4} = 5.43e-7 m^2/s, α_{PI} = 3.16e-7 m^2/s) can transport more heat if the volume of the materials are equal, which increases the intensity of the condensation. The current results give answer for the contradictory ECM behaviour between Silver-polymer on polyester-substrate (higher MTTF) and Copper on PCB (lower MTTF) during THB tests [12]. However, according to my results the ECM ability of Ag is higher (lower MTTF) than Cu. The root cause of the MTTF difference is about the different MTTC, which parameter depends mainly on the different substrate types. So, the ECM influence of the metals (MTTD) is not so relevant in those cases.

Related Publications: L2, R4

[1] The *thermal diffusivity* can be calculated according to the following equitation:

$\alpha = \frac{\lambda}{\rho * C_S}$, where

λ is thermal conductivity [W/m*K], ρ is density [kg/m^3], C_S is the specific heat capacity and α is thermal diffusivity [m^2/s].

III. Thesis

I have shown that the ranking position of copper and lead are not obvious, the ranking reported earlier (Ag>Pb>Cu>Sn), correlated with the solubility of metal hydroxides should be modified to in some cases: Ag>Cu>Pb>Sn. In the case of lead-bearing solder alloy, the explanation is based on the formation of eutectic alloy and the modified anodic dissolution rate. In the case of copper, the oxidation state of the surface influences the dissolution.

Discussion: I have shown that the Mean-Time-To-Failure rates were significant different between Copper and Hot Air Solder Leveling (HASL) surface finish. An accepted ranking of the ECM susceptibility of silver, copper, tin and lead is the following: Ag>Pb>Cu>Sn (Silver is the worst) [9]. This ranking, which refers to time to failure was correlated with the different solubility product constant of different metal hydroxides (e.g.: $Sn(OH)_2$). However, according to my experiment the following ranking was established: Ag>Cu>Pb(HASL)>Sn. So the ranking place of Cu and Pb was changed. One cause of this change can be found at the difference between the Pb-alloy compositions. On the other hand different copper ions Cu^{1+} or Cu^{2+} were formed during ECM processes depending on the *oxid-layer* on copper surface. I have shown that the *oxid-layer* of copper has strong influence on ECM: In the case chemically cleaned ("oxide-free") copper mainly Cu^{1+} ions were formed instead of Cu^{2+} ions during ECM processes.

Related Publications: L3, R2, R5

IV. Thesis

I have shown that the electrochemical migration behaviour of some Micro-alloyed Low Ag Content Solders (eg.: SAC0807) has significant reliability risk comparing to the Sn63Pb37 lead-bearing solder and also to the widely used SAC305 solder used in microelectronics under chloride solution. I have shown the relationship between the Mean-Time-To-Failure (MTTF) and the oxidation velocity related to electrochemical corrosion: The higher oxidation velocity (SAC0807: ~50 nm/h, SAC0307: ~20 nm/h) means the lower MTTF (SAC0807: ~ 178 s, SAC0307:~ 574 s) and vice versa.

Discussion: During the electrochemical corrosion and migration processes, basically two concurrent anodic reactions playing important rule: Oxide layer growth on the metal surface and the anodic dissolution of the metal forming metal ions. If the growth of the passive (metal-oxid) layer is fast and stable enough it can hinder or even stop the anodic dissolution process. Later, the formed passive layer on the anode might totally or locally be destroyed. The destruction velocity of the passive layer and it's inhomogeneity both in vertical and in horizontal directions influences the anodic dissolution speed of metal ions. I have investigated on Sn based low Ag content micro-alloyed solder alloys by XPS method and found very inhomogeneous oxide front in both (vertical and horizontal) directions. It can be supposed that this inhomogeneous oxide front was caused by the so called pitting corrosion, hence only pits were found on the uniform oxide layer. Pitting corrosion is most commonly induced by chloride ions or other halides. The pitting corrosion ability depends mainly on the elemental composition of the solder alloy. *Deeper pits* produce more metal ions (*higher oxidation velocity*) and therefore the higher concentration of metal ions can migrate and formed with higher probability or faster dendrites and finally shorts (*lower MTTF*) than in case of lower pits.

Related Publications: L4, R3

Benefits of the scientific work

The results provide extended information about the ECM phenomenon. This is useful for a better understanding of the entire ECM process and thus, for creating an even more realistic model, which ensures improved reliability in electronics design.

Furthermore, I expect that the results will be useful for the electrical industry in choosing the proper materials and in setting up the optimal technological parameters during manufacturing as well. Some of the results are already being utilized by Robert Bosch Ltd. in Stuttgart and by Continental Automotive Hungary Ltd.

This work is connected to the scientific program titled "Development of quality-oriented and harmonized R+D+I strategy and functional model at BME", Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002 – NNA and the „Talent care and cultivation in the scientific workshops of BME" project, which is supported by the grant TÁMOP-4.2.2.B-10/1--2010-0009. Furthermore, the work supports the aims of the Campus Hungary Program as well. Later, I have worked at the National Institute for Materials Science (NIMS) in Japan (for 7 months), engaged in electrochemical migration investigations.

List of Publication

Publication related to Thesis

Journal papers

[L1] **B. Medgyes,** B. Illés, R. Berényi and G. Harsányi, "In situ optical inspection of electrochemical migration during THB tests", JOURNAL OF MATERIALS SCIENCE-MATERIALS IN ELECTRONICS, Vol. 22, No. 6, pp. 694-700 (2011), IF: 1.070

[L2] **B. Medgyes,** B. Illés and G. Harsányi, "Effect of Water Condensation on Electrochemical migration during THB tests", JOURNAL OF MATERIALS SCIENCE-MATERIALS IN ELECTRONICS, Vol. 24, No. 7, pp. 2315-2321 (2013), IF: 1.486*

[L3] **B. Medgyes,** B. Illés and G. Harsányi, "Electrochemical migration behaviour of Cu, Sn, Ag and Sn63/Pb37", JOURNAL OF MATERIALS SCIENCE-MATERIALS IN ELECTRONICS, Vol. 23, No.2, pp. 551-556 (2012), IF: 1.486

[L4] **B. Medgyes,** B. Illés and G. Harsányi, "Electrochemical Migration Behaviour of Micro-alloyed Low Ag Content Solders in NaCl Solution", PERIODICA POLYTECHNICA-ELECTRICAL ENGINEERING, 57:(2) pp. 49-55 (2013)

Referred Conference papers

[R1] **B. Medgyes,** R. Berényi, L. Jakab and G. Hársanyi, "Real-time monitoring of electrochemical migration during environmental tests" Proc. of the 32nd IEEE International Spring Seminar on Electronics Technology (ISSE), Brno, Csehország, pp. 1-6 (2009)

[R2] **B. Medgyes** and B. Illés, "Contradictory Electrochemical Migration Behavior of Copper and Lead", Proc. of the 34th IEEE International Spring Seminar on Electronics Technology (ISSE), Tatranska Lomnica, Szlovákia, pp. 206-211 (2011)

[R3] **B. Medgyes,** D. Rigler**,** B. Illés, G. Harsányi and L. Gál, "Investigating of Electrochemical Migration on Low-Ag Lead-Free Solder Alloys" Proc. Of the 18th IEEE International Symposium for Design and Technology of Electronic Packaging (SIITME), Alba Iulia, Románia, pp. 147-150 (2012)

[R4] **B. Medgyes,** B. Illés and L. Gál, "Measurements of Water Contact Angle on FR4 and Polyimide Substrates relating Electrochemical Migration" Proc. of the 36th IEEE International Spring Seminar on Electronics Technology (ISSE), Alba Iulia, Románia, pp. 1-4 (2013)

[R5] **B. Medgyes**, B. Illés, D. Rigler, M. Ruszinkó and L. Gál, "Electrochemical Migration of Copper in Pure Water used in Printed Circuit Boards", Proc. Of the 19th IEEE International Symposium for Design and Technology of Electronic Packaging (SIITME), Galati, Románia, pp. 267-270 (2013)

Other publications

Referred Conference papers

[R6] **B. Medgyes** and B. Illés, ”Investigating SIR of Cu, OSP, iSn and HASL Surface Finishes by THB Test”, Proc. Of the 17th IEEE International Symposium for Design and Technology of Electronics Packages (SIITME), Timisoara, Románia, pp. 345-348 (2011)

[R7] **B. Medgyes** and G Ripka, ”Qualifying Methods of Conformal Coatings used on Assembled Printed Wiring Boards”, Proc. Of the 30th IEEE Int. Spring Seminar on Elctronics Technology (ISSE), Cluj-Napoca, Románia, pp. 429-433 (2007)

Not Referred Conference papers

[K1] **B. Medgyes,** ”Qualifying Lead-Free Solder Joints on Printed Circuits Boards”, International Symposium for Design and Technology of Electronic Packages (SIITME), Brasov, Románia, pp. 385-388 (2008)

[K2] **B. Medgyes,** ”Life-time tests on printed circuit boards and qualifying lead-free solder joints”, International microelectronics and packaging conference (IMAPS), Pułtusk, Lengyelország, pp. 282-287 (2008)

[K3] **B. Medgyes,** ”Investigating Electrochemical Migration on Assembled Printed Circuit Boards coated by Conformal Coating”, International Symposium for Design and Technology of Electronic Packages (SIITME), Baia Mare, Románia, pp. 32-35 (2007)

Hungarian Journal paper

[M1] **B. Medgyes,** ”Szerelt áramkörök alakkövető bevonása: Conformal Coating”, ELEKTRONET, Vol. 1, No. 1, pp. 35-36. (2007)

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[12] P. Bojta, P. Németh and G. Harsányi, "Migration Reliability Comparison of Interconnection Substrates: Polymer Thick Films Seem Better than Regarded?", Proc. of the 14th European Microelectronics and Packaging Conference (IMAPS), pp. 189-195 (2003)

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