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Microstructure and elemental composition of electrochemically formed dendrites on lead-free micro-alloyed low Ag solder alloys used in electronics

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ABSTRACT

The Electrochemical Migration (ECM) behaviour of lead-free, micro-alloyed, low Ag solder alloys was investigated using Scanning Transmission Electron Microscopy (STEM), Energy Disperse X-ray Spectroscopy (EDS) and electron diffraction methods. Different solder alloys were investigated by Water Drop (WD) tests to stimulate ECM failure mechanism. After WD tests, differently structured dendrites were formed depending on the solder alloy types. The results showed that micro-alloying components (e.g. Sb) also played role during the ECM processes. The novelty of this study is the demonstration that Sb can take part in the ECM process; the ECM model of Sb is also discussed.

1. Introduction

The quality and reliability of solder alloys are important factors for microelectronic applications. According to the Restriction of Hazardous Substances (RoHS) directive of European Union, lead bearing solders had to be replaced with lead-free ones [1]. In this context, alternative binary alloys had been examined as replacements for Sn–Pb solders, such as near-eutectic Sn–Ag, Sn–Cu, and Sn–Zn alloys [2]. However, ternaries (Sn–Zn–Ag, Sn–Zn–In, etc.) and even quaternary alloys (Sn–Zn–Ag–Al, Sn–Ag–Bi–Cu, Sn–In–Ag–Sb) had been studied as candidates for lead-free solders [3–6].

The reliability investigation of lead-free solders is still a huge challenge in microelectronics. One of these important topics is about the Electrochemical Migration (ECM) failure phenomenon, which is a kind of manifestation of electrochemical corrosion mechanism as well. The common behaviours of the ECM phenomenon involve the presence of moisture on conductor–dielectric–conductor systems under bias voltage, the electrochemical process and the metallic dendrite growth [7]. The process is driven by the electric field between the anode and the cathode. Dendrite growth occurs as a result of metal ions being dissolved into a solution from the anode and deposited at the cathode, thereby growing needle- or tree-like formations. The dendrites reaching the anode cause short-circuits in the electronic circuits, which may lead to a catastrophic failure.

The description of the ECM phenomenon has still many open questions such as undefined reaction and process model elements. The existing models cannot adequately describe the whole assortment of the ECM phenomena. These electrochemical processes occur in very small volumes of electrolytes (~μl), furthermore, the processes are neither stationary in time nor homogeneous in space. Therefore, only empirical models exist [8,9].

Many research reports can be found about ECM investigations carried out on various lead-free solder alloys [10–12]. There are also other publications which concentrate on different reliability issues like solderability, intermetallic compounds or tensility and wettability properties of novel lead-free micro-alloyed low Ag content solders [13–15]. Nowadays, a new tendency in the development of the Sn–Ag–Cu (SAC) solder alloys is to reduce the silver content and therefore reduce the price as well. The low silver content have to be candidate with micro-alloying elements like antimony, bismuth, cobalt, nickel etc. These novel SAC alloys are the so called "Lead-free Micro-alloyed low Ag Solder Alloys". In the micro-alloyed low Ag solder alloys the tin content is relative high (over 98 wt%), while the silver content is much lower (under 1 wt%) than in case of the traditionally SAC alloys (Sn ~96 wt%, Ag ~3 wt%, Cu ~1 wt%). Our former publication [16] was the first to report about some ECM results of the latest lead-free micro-alloyed low Ag content solders. In that study [16], mainly the corroded anode surface was investigated by X-ray Photoelectron

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Spectroscopy (XPS), which provided information about the anodic dissolution processes which take place during ECM and the Mean-Time-To-Failure data (MTTF) during water drop and environment tests. According to [16], an ECM ranking of lead-free solder alloys can be established (Sn96.5Ag3Cu0.5 has the highest ECM susceptibility to short formation):

$$\mathrm{Sn96.5Ag3Cu0.5} \geqslant \mathrm{Sn98.4Ag0.8Cu0.7X0.1} \geqslant \mathrm{Sn95.5Ag4Cu0.5} \geqslant \mathrm{Sn98.9Ag0.3Cu0.7X0.1} \quad (1)$$

where X are the micro-alloy elements in weight%.

According to Eq. (1), some types of the low Ag content lead-free micro-alloyed solders (e.g. SAC0807) showed a relatively high susceptibility for ECM, which may pose high reliability risk in the electronic devices.

On the other hand, there is only little information available about the composition and structure of the dendrites formed, which are also very characteristic for the ECM behaviour and can provide additional information about the deposition processes at the cathode. The dendrites formed by ECM are usually investigated by Optical Microscopy or by Scanning Electron Microscopy and Energy Disperse Spectroscopy (SEM–EDS) [17–21]. Additionally, there are also newer reports which used Transmission Electron Microscopy (TEM) and EDS for different dendrite investigations in the nanometer range [22–25]. However, no reports were found about the TEM–EDS investigation on dendrites formed from lead-free micro-alloyed low Ag content solders used in microelectronics.

In this paper the dendrites of different lead-free micro-alloyed low Ag content solders were investigated by TEM–EDS caused by ECM in a NaCl solution. Furthermore, electron diffraction measurements were also carried out to obtain more information about the elemental composition of the dendrites. The dendrites were grown using the so called WD test.

2. Experimental

2.1. Dendrite growth during WD test

In order to stimulate ECM processes (which resulted in dendrites – see Fig. 1), WD tests were carried out on different lead-free micro-alloyed low Ag content soldered double comb patterns. The patterns were designed according to the IPC-B-24 test board with the following main parameters; the line width of the conductor stripes was 0.4 mm with a gap size of 0.5 mm on an FR4 (fibreglass reinforced epoxy) substrate. The patterns were formed by conventional photolithography and wet etching processes. The Cu base conductor was coated by immersion Sn that is commonly used for further reflow soldering processes. During this study, the following lead-free micro-alloyed low Ag content solders were investigated (concentration of the elements are in weight%):

1. Sn98.9Ag0.3Cu0.7 (SAC0307) and 0.1% of micro-alloy(s),
2. Sn98.4Ag0.8Cu0.7 (SAC0807) and 0.1% of micro-alloy(s).

The solder pastes were printed by a 150 μm thick stainless steel stencil and were reflowed according to a lead-free (190 °C, 210 °C (90 s), 240 °C (30 s) soldering temperature profile suggested by the supplier. In order to avoid the influence of fluxes [26], the same type of flux was applied in all cases.

During the WD tests (see platform in Fig. 1), a droplet of 15 μl of 3 wt% NaCl was placed by a pipette onto the double comb patterns and then U = 10 VDC was applied (R = 1 kΩ as a current limiter). The NaCl solution simulates the seawater. Finally, the dendrites formed were post-processed for TEM–EDS investigations.

2.2. Sample preparation for TEM investigation

Initially, the used method for TEM sample preparation was applying a focused ion beam (FIB) on the dendrites on the FR4. However, it was not useful due to the very fragile nature of the dendrite structure and the poor adhesion force between the dendrite and the FR4. Therefore, in this investigation a simple method was adopted in which the dendrite was carefully transferred onto a Mo TEM-grid (200 mesh) coated with a thin (10 nm) carbon layer. Since the dendrite thickness was in the nanometer scale, it was found that it could directly be used for the TEM analysis without any post sample preparation procedure. The procedure of sample preparation contains four steps; Step (1) Removing the dendrite by using scotch-tape (Fig. 2), Step (2) Set the dendrite as in Fig. 3 was shown, Step (3) Immerse them in toluene for several hours, Step (4) Pick up whole from toluene and remove the tape, c-ring and paper.

The TEM (JEM-2100F, JEOL) instrument was used in Scanning-mode (STEM) with a spot size of 1 nm (camera distance was 40 cm) to investigate the micro- and nanostructures. The EDS system (EX-23003BU, JEOL) and electron diffraction measurements (focus distance 120 cm) were also used to identify the different elemental compositions of the dendrites.

3. Results

In Figs. 4 and 5, STEM micrographs are shown with labelled EDS lines and spots. In both cases (SAC0307 and SAC0807), EDS lines (L1, L2 and L3, L4) were measured and each line has 5–5 measurement points.

The results of EDS points are shown in Tables 1 and 2. According to the EDS results, a micro-alloy element; antimony have participated in the electrochemical processes. The presence of Sb is an unexpected result, since there are no reports of it in the ECM literature. Therefore, the ECM behaviour of Sb will be discussed below.

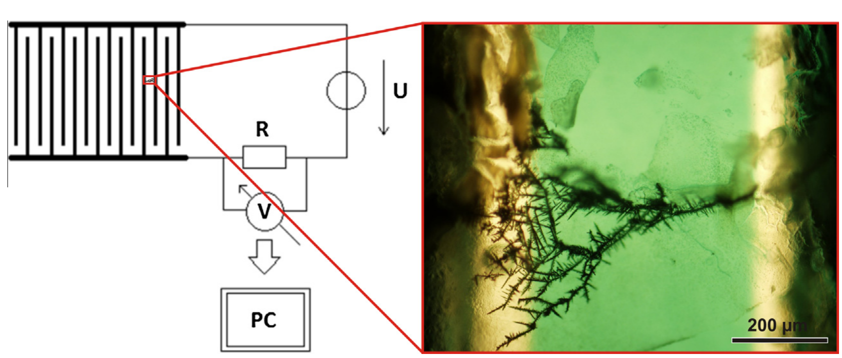

Fig. 1. Test platform form WD test (left, R = 1 kΩ) and a SEM micrograph of dendrites after WD test (right).