Effects of electrolyte towards copper wire metallurgical interconnection in semiconductor

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Abstract. Copper (Cu) wire has been extensively used in the semiconductors industry to replace gold wire because of its cost-effectiveness and high performance. However, it has a massive challenge because of its high oxidation rate, high hardness, and high susceptibility to corrosion which is time-sensitive under environmental conditions. One of the attractive factors to investigate is the electrolyte used in the assembly process of copper wire. However, these electrolyte chemicals may potentially affect the quality of the copper wire bond's metallurgical interconnection, manifesting as copper corrosion. Therefore, this paper will investigate the mechanism of the electrolyte reaction and the chemicals. In addition, the metallurgical morphology of the copper wire observes through electron microscopy. The results suggest that corrosion occurs with a specific time rate, electrolyte type-dependent and metallurgical interconnection system. The Copper wire bonded on silver (Ag) plated lead frame (Cu-Ag-Cu) interconnection experiences a significant morphological change in most compared with other electrolyte systems. Furthermore, since it is a bimetallic element (Cu and Ag) thus, the corrosion type is galvanic.

1 Introduction

The best wire material for wire bonding technology probably is gold wire, as it provides a good bonding process and reliability performance [1-3]. However, the packaging industry is searching for an alternative material for wire bonding [4]. Among the candidate materials that attracted attention are copper wire, silver wire and aluminium wire. Copper is the cheapest alternative with relatively good mechanical and electrical properties and is widely opted in fine-pitch applications and high-speed devices. Silver wire has also been used in fragile packages with good electrical and thermal conductivity but has not been popular because of its higher price than Cu [1]. As for Aluminium wire, despite its oxidation resistance behavior, it is not usually opted for because of its poor free air ball (FAB) formation [5]. Apart from the functionality and reliability of wire bonding, corrosion aspects also play a crucial role in determining the lifespan of the microelectronics packaging. There are many papers for the past thirty years that have been focusing on corrosion in the microelectronics. Corrosion in the semiconductor industry has an impact on the quality and reliability of product performance. However, the classification of corrosion forms is arbitrary because many types of corrosion are interrelated, and it is impossible to have the exact distinction. The corrosion category in microelectronic devices is according to the reaction mechanisms and the visual characteristics of the morphology of the corrosion attack [6-9]. The one aspect related to the corrosion phenomena that motivate this works is the effect of chemicals used in the assembly process, which become electrolytes towards bi-metal metallurgical interconnection. Understanding these factors contribute to the corrosion mechanism is essential in dealing with microelectronic corrosion.

The critical elements of galvanic corrosion are the anode, cathode, moisture, electrolyte, and current. Fig. 1 shows a typical galvanic cell involving different metals with a distinct potential difference. Several studies suggested that galvanic corrosion occurs when an electrochemical potential difference between two metals and electrolytes [10] happens in the ball bond and the wedge bond intermetallic region. The objectives of this paper are to investigate the mechanism of the electrolyte reaction and the chemicals. The approach is through the lab experiment subjecting the metallurgical system to several electrolyte chemicals. This paper reports some experimental observations to understand the corrosion mechanism due to the presence of electrolyte onto bi-metal metallurgical interconnection, using Cu wire and Ag-finished leadframe. This involved lab-scale experiments using similar materials and chemicals in the standard packaging process.

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2 Methodology

This work is focused on the combination of two types of wire bonding metallurgical interconnection systems, the Cu-Ag and Cu-Cu systems. Commercial Cu wire with diameter of 23 μm has been used. Cu leadframe plated with Ag was used to produced Ag-finished for Cu-Ag system while bare Cu leadframe was used for Cu-Cu system. For the Cu-Ag system, the wire was then thermosonically bonded on the leadframe to form bi-metal metallurgical interconnection of wire bonding. For Cu-Cu system, bonding process via thermosonic of Cu wire was done into a bare Cu leadframe to form Cu-Cu bond. The wire bonding of the first bond and the wedge bond processing parameter are in line with the standard industrial practice in wire bonding process. Four different types of electrolytes have been prepared, which are potassium hydroxide (KOH), methane sulfonic acid (MSA), water (H2O) and sodium chloride (NaCl), with different level of concentration of 3% and 40%. To observe corrosion behaviors, the sample was soaked in the beaker containing of different electrolyte. Bare Cu wire without bonding was used as a control sample. The samples were soaked and kept for daily observation up to 11 days. Each of the sample which was taken out from electrolyte will not re-soaked to ensure continuation of corrosion behaviours. The experiment was also carried out in a closed container. The setup of the experiment is shown in fig. 2.

Observation of the surface and morphological changes has been made using scanning electron microscope (SEM) (Model: JEOL, JSM, 6010LV). Qualitative analysis has been carried out on the SEM images to investigate the effect of the electrolyte on the corrosion behaviors. The samples were taken out on day 3, 7 and 11 individually and dried out before being observed under the SEM. The qualitative analysis will use the colour coding as shown in Table 1 to indicate the level of the corrosion effect on the microstructure of the wedge bond for both Cu wire systems.

| Colour Code | Level indicator | Description of wedge morphology          |
|-------------|-----------------|------------------------------------------|
| 0           | Good            |                                          |
| 1           | Minor change of morphology |
| 2           | Minor change of morphology |
| 3           | Minor change of morphology |
| 4           | Minor change of morphology |
3 Results and Discussion

Fig. 3 shows the images of the two type Cu wire systems bonded to the substrate, Cu-Ag and Cu-Cu after immersion test. These SEM images focus on the top view of the wedge bond wire bonding, after 3, 7 and 11 days of immersion. The colour coding with numerical value is attached at the topside of the SEM image is represent qualitative analysis of the surface morphology with respect to the corrosion activity on the surface due to the immersion test.

The Cu-Ag system in (i) is not being soaked in any electrolytes and act as a control. The control image is important to established qualitative study in the morphology of corroded surface. Then qualitative analysis has been carried out using colour contrast in fig. 3 to indicate changes with respect to the control system. The colour code represents severity of corroded Cu wedge, ranking from 0 (good bonding with 100% wedge intact as per control), to 10 (severely degraded Cu wedge with missing wedge structures). There are no changes seen for the control system. And based on the SEM photos, no severe impact observed in (iv) which uses H2O as an electrolyte. For both systems in (i), (ii) and (iii), not many changes observed until day 3. A significant change on the copper wedge on day 7 can be seen in (ii) which uses NaCl as its electrolyte where some of the copper masses are degraded and the wedge shows deformation in shape. This condition continues until day 11, where more copper mass degradation can be seen. More severe copper disintegration is seen in Cu-Ag system than that of Cu-Cu system.

Lesser impact seen on (i) in KOH but is more severe in Cu-Ag system with higher concentration of KOH. No many changes seen in Cu-Cu system where most of the copper mass are still intact with the wedge. Least impact is seen in (ii) with MSA as electrolyte in both systems, where the condition of the copper wedge is most likely the same compared with day 3, and with the control.
Thus, the results obtained give clearer understanding on the galvanic corrosion behavior. Cu- Ag system morphological changes as discussed above demonstrates galvanic corrosion as there are two dissimilar metals in contact with a presence of electrolyte. This forms an electrochemical cell as there is a potential difference between the two metals. The metal with a more negative potential becomes the anode, thus is corroded by electrochemical reactions. Referring to the electrochemical potential series in Table 2, Cu is more negative than Ag, thus become the anode which loses electrons and undergoes corrosion. Therefore, there is a degradation and disintegration of copper wedge, indicating copper corrosion. The reaction rate of this corrosion also depends on the concentrations of the contaminants. We can see faster corrosion occurs in 40% KOH and NaCl than in 3% of the electrolyte [7].

| Electrolyte | Concentration | Cu- Ag | Cu- Cu |
|-------------|---------------|--------|--------|
| (i) KOH     | 40% w/v       | 5 6 9  | 1 3 6  |
|             | 3% w/v        | 5 5 6  | 1 3 5  |
| (ii) NaCl   | 40% w/v       | 5 8 9  | 5 7 8  |
|             | 3% w/v        | 5 6 8  | 5 5 6  |
| (iii) MSA   | 40% v/v       | 1 4 5  | 1 1 3  |
|             | 3% v/v        | 1 1 4  | 1 1 2  |
| (iv) H₂O    | Nominal       | 1 2 3  | 1 2 2  |
| (v) Control | No immersion  | 0 0 0  | 0 0 0  |

Fig. 3. Morphological change of different Cu wire system in (i) KOH, (ii) NaCl, (iii) MSA, (iv) H₂O and (iv) Normal Cu- Ag wire with no immersion.

| Electrode | Oxidation reaction | E°(V) |
|-----------|--------------------|-------|
| Mg        | Mg → Mg²⁺ + 2e⁻    | +2.36 |
| Al        | Al → Al³⁺ + 3e⁻    | +1.68 |
Zn $\rightarrow$ Zn$^{2+}$ + 2$e^-$ +0.76
Fe $\rightarrow$ Fe$^{2+}$ + 2$e^-$ +0.44
Pb $\rightarrow$ Pb$^{2+}$ + 2$e^-$ +0.13
Cu $\rightarrow$ Cu$^{2+}$ + 2$e^-$ −0.34
Ag $\rightarrow$ Ag$^{2+}$ + 2$e^-$ −0.80
Pd $\rightarrow$ Pd$^{2+}$ + 2$e^-$ −0.92
Au $\rightarrow$ Au$^{3+}$ + 3$e^-$ −1.40

The reactions on both anode and cathode are summarized as following equations:

\[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \] (1)
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] (2)
\[ Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \] (3)

Equation 1 shows the reaction at the anode whereby Cu loses electrons to become Cu ions. This equation indicates oxidation reaction which is also known as corrosion. Porous surface at the beginning of the experiment with Cu-Ag system and missing wedge implies that corrosion has taken place and degrades the copper mass from the wedge adhesion. This study imitates the actual condition in semiconductor industry when there is a presence of electrolyte in the environment that will affect the copper wire metallurgical bonding. Cu-Ag system is susceptible to galvanic corrosion when exposed to contaminants that will result in degradation of its copper wedge mass and will affect its reliability with time. This can lead to issues such as open circuit that will fail the workability of the product [11]. This can also happen in Cu-Cu system where some electrolytes play a role in affecting the morphological structure of the wedge bond. This study also shows that it takes a period for corrosion to take place to attack the metal part and slowly degrading the large copper mass, and eventually disrupting its electrical performance. In the semiconductor industry, corrosion might take a longer time to occur depending on the robustness of the package and process, and application of the product. In other cases, such as Cu- Al bonding which also known as intermetallic bonding, galvanic corrosion can also take place with Al acting as the anode. This is also commonly known as bond pad corrosion where the Al pad is the one losing electrons, thus become corroded. This issue has been widely discussed than the wedge corrosion itself as its involving metals with a large potential difference. The larger the potential difference between two metals, the more rapidly the anode will undergo corrosion. As discussed by Gan et. al, this IMC corrosion results in cracking of the interface due to outgassing of hydrogen gas from the presence of moisture (electrolyte) in the system which causes open circuitry [11].

4 Conclusions

Copper wire bonding technology is a typical integrated circuit packaging solution for contemporary microelectronics technology is facing significant issues of corrosion. This is a systematic study that involves a lab work to represent Cu wire bond system in real semiconductor industry. The data indicate that Copper wire bonded on silver (Ag) plated lead frame (Cu-Ag) interconnection experience a significant morphological change as compared with Cu-Cu system, in most of the electrolyte system used. This follows galvanic corrosion model due to the bimetallic element (Cu and Ag) in the metallurgical interconnection. Both Cu wire system experiences the most severe effects of corrosion when soaked in NaCl. This initial analysis also proves that these electrolytes are a significant factor causing corrosion, that must be eliminated to ensure no reaction can take place to further react with sensitive copper material that will adversely affect its quality and reliability. The longer the soaking time, the corrosion activity occur more significantly. In term of electrolyte, corrosion activity is more active in KOH and NaCl as compared to MSA and H$_2$O. Corrosion can also be prevented by using same metals to eliminate the potential difference. But it is crucial to ensure usage of same metals with same purity as dopants can result in creating slight or wide potential difference that can still, eventually make way for corrosion to occur.

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