Kinetic study of eutectic Sn-3.5Ag and Electroplated Ni metallization in flip-chip solder joints

Hsiao-Yun Chen and Chih Chen*

Department of Materials Science and Engineering, National Chiao Tung University, Hsin-chu 30010, Taiwan, Republic of China

Absract

It is well known that Ni and its alloys possess a lower reaction rate with Sn than Cu and Cu alloys. Therefore Ni-based under bump metallization have attracted attention in recent years. In this study, the diffusion-controlled reaction between eutectic Sn-3.5Ag flip chip solder joints between electroplated-Ni (EP-Ni) and electroless-Ni (EL-Ni) has been investigated. Morphology and growth kinetics of the formed Ni_3Sn_4 are study under different reflow temperatures, durations and times. The growth rates and the formation activation energy of Ni_3Sn_4 IMC were estimated with EP-Ni and EL-Ni, respectively. The obtained data showed that the Ni_3Sn_4 in the Sn-3.5Ag filp chip solder grow much faster with EP-Ni than EL-Ni UBM under the same condition. In summary, we can conclude that the slow reaction rate of EP-Ni provided a well-attached contact at the interface after 20 minutes reflow process and is better compare with EL-Ni UBM at the substrate.

* Corresponding author. Tel.: +886-35731814; fax: +886-357247

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I. Introduction

Due to increasing environmental concerns, the microelectronics industry is replacing Pb-containing solders by Pb-free solders. In recent publications, SnAg-based solder has emerged as one of the most promising Pb-free candidates to replace the conventional eutectic SnPb solder in flip-chip technology [1-3]. A reliable solder joint can be formed by a metallurgical reaction between molten solder and under-bump metallization (UBM) on a chip or metallization on a substrate, which produces stable IMCs at the joint interfaces [4]. The growth of these intermetallic compounds (IMC) can strongly affect the mechanical reliability of the solder joints [5-7]. As the result, selection of appropriate under bump metallization (UBM) plays an important role in developing a reliable joint, especially so with the adoption of the lead-free solders. Copper and nickel are the two common UBM materials used in the packaging industry. Copper reacts with the solder alloy very quickly and provides excellent wetting[8]. Yet, the fast consumption rate of the Cu UBM may cause spalling of the interfacial IMC after longer reflowing time[9-11]. This spalling issue became aggregated with the switching to Pb-free solders, because Sn-based Pb-free solders react with Cu at a much higher rate. Instead, Ni-based under bump metallizations, such as electroless Ni-P alloy and pure Ni, have attracted attention in recent years because of their good wettability [12], good diffusion barrier ability and slow reaction rate with solders [7, 13]. Many studies have been published on the interaction between Ni-P and Sn-based solders [14-24]. They mainly investigated the formation and growth of IMCs at the interface between molten solder and Ni-P UBM, solder reaction-assisted crystallization of Ni-P alloy, and the influences of the IMCs on the mechanical properties of the solder joints.

Most of previous works are mainly focused on solder/Ni-P reaction. However, little studies have been done on the interfacial reaction between molten solder and electroplated Ni.[25-29] The comparison between molten solder and the Ni-based metallization at the same time in flip chip solder joints has not been investigated, neither nor their growth kinetics. The consumption rate of the EP-Ni has not been measured yet, and the kinetics of the interfacial reaction is not clear.

II. Experimental procedure

Their schematics are shown in Figure 1. Figure 1 (a) shows the flip-chip package sample for interfacial-reaction study, whereas bumped-die sample is adopted to facilitate the shear test on the solder bump as shown in Figure 1 (b). On the chip side for both samples, titanium of 0.1μm was sputtered onto the oxidized Si wafer to serve as a good adhesion layer. Copper of 0.5 μm thick was then sputtered on the Ti layer and served as a seed layer for the subsequent electroplating process. Then the Cu or Ni layer was electroplated on the Ti/Cu layers. Photolithography was applied to define the contact opening on the chip-side for solder electroplating of eutectic SnAg solder. The solder bumps were formed by reflowing in an infrared oven at 260 °C for about 1 min. For flip-chip package samples, the bumped dies were then mounted to a FR5 substrate, in which the pad metallization on the substrate side was 5 μm electroless Ni on the 30 μm thick Cu lines. The solder bumps experienced another reflow during the mounting process. For metallurgical reactions at the liquid-state reactions, flip-chip samples were reflowed at 230°C, 240°C and 250°C for 5 min, 10min, 15min and 20 min, while bumped-die samples were reflowed for 1, 5 and 10 times, in which about 1 min. The compositions of the solder joints and the IMC were analyzed quantitatively by energy dispersive spectroscopy (EDX) and an electron probe microanalyzer (EPMA, JXA-8800M, JEOL).

Results

3.1 Growth of IMC and Ni consumption rate

The flip-chip samples provide a direct comparison between the EP-Ni/solder and EL-Ni/solder interface. Figure 2 (a) shows the cross-sectional SEM image for the as-fabricated flip-chip samples, in which the EP-Ni/solder interface located on the chip side, and the other interface is on the substrate side. The bump height is about 75 μm. The enlarged SEM images for the two interfaces are illustrated in Figures 2(b) and 2(c), respectively. Due to the fabrication processes described in the experimental section, the interface of EP-Ni/solder underwent two-times reflows, which corresponds to two-minute duration of liquid-state reaction. On the other hand, the interface of EL-Ni/solder only experienced one-minute liquid-state reaction. The IMC morphology appears to be quite different. Column-type IMCs are observed on the EP-Ni surface, where as needle-type IMC formed on the EL-Ni surface. The height of the column-type IMC is more uniform than that of the needle-type IMC. The IMCs on the two interfaces were identified to be Ni_3S_4.

It is found that the initial IMC growth rate is slower on the EP-Ni side. As showed in Figure 2(b) and 2(c), the IMC grown on the EP-Ni/solder interface was measured to be 0.94 μm, which is thinner than that grown on the EL-Ni/solder interface (1.31 μm). Since the EP-Ni/solder experienced one more minute reflow than the EL-Ni/solder interface, the IMC formation rate at the EP-Ni side is about 1.4 times slower than that at the EL-Ni side.

The bumped-die samples were employed to measure the IMC growth rate and EP-Ni consumption rate, at typical reflow temperature of 260°C for eutectic SnAg solders. Figure 3(a) shows the cross-sectional SEM image for the as-fabricated SnAg bumps on EP-Ni UBM, which underwent one reflow, and the enlarged one is shown in Figure 3(b). After reflowed for 10 times, the column-type IMC still attached well with EP-Ni UBM with growing much thicker which is as shown in Figure 3(c). Be more accurately considered with the reliability of EP-Ni, after 10 times reflowed there is yet 2.2 μm EP-Ni remained as obtained from Figure 4(a) and 4 (b). Only about 0.8 μm of EP-Ni was consumed after reflowed at 260°C for 10 minutes and 2.6 μm IMC is obtained to bond solder/UBM interface. The precise consumption rate of EP-Ni is estimated to be 1.33 x 10^{-3} μm/sec under this reflow condition within 10 min.

For flip-chip samples, the analyzed average IMC values are listed in Table 1 versus with temperature and time durations. The corresponding SEM images of IMC thickness variation with time and temperature are shown in Figure 5(a) to 5(c). It is known that the growth kinetics of the continuous IMC layer (Ni_3Sn_4) can be expressed with an empirical power law describing the average IMC thickness (h) as a function of time (t) and temperature (T):

$$h(t,T) = h_0 + k_h \exp\left(-\frac{Q_h}{RT}\right) t^{1/n}$$

The best fit of the experimental data, which is shown in Figure 6 (a) yielded n values of 4.5 and 3.13 for EP-Ni and EL-Ni systems respectively, which are somewhat similar to the n values of 4.55 and 4.69 that reported by Ghosh for Ni_3Sn_4 scallops formed in SnAg/Ni samples at 230-290˚C up to 5 min. The activation energies are 25 KJ/mol of EP-Ni interface, and 38 KJ/mol of EL-Ni interface respectively.

Discussion

IMC growth kinetics in liquid state reaction

During soldering process, it involves several interface processes, such as phase nucleation, atomic transfer across the interface, creation and/or annihilation of point defects, if any, and dissolution into the molten solder. Therefore, the kinetic parameters evaluated from the experimental data may have a complex meaning. The thickening process of Ni_3Sn_4 as shown in Fig. 6(a) for both EP-Ni and EL-Ni systems differs form diffusion-controlled growth, which predicts $t^{1/2}$ growth kinetics [26,31,32]and from a scallop coarsening by a ripening process refers to $t^{1/3}$ [33]. These results are somehow familiar to those reported by Ghosh[26]. According to Ghosh, the thickening kinetics of Ni_3Sn_4 scallop is related to the radial growth kinetics, and grain boundary diffusion may play an important role in the thickening kinetics Since Ni_3Sn_4 scallop are individual grains. Kang and Ramachandran [34] reported the interfacial reaction kinetics between liquid Sn and bulk Ni. There are three kinetic regimes for intermetallic growth, where Ni_3Sn_4 was the dominant phase, in the temperature range of 300–513 °C: initial with n=1.85, intermediate with n=8.33, and final with n=1.59. Kang, Rai, and Purushothaman[35] reported the interfacial reaction between electroplated Ni on Cu and various solders, but did not report any kinetic parameter. Gur and Bamberger [36] reported that both thickening and grain growth kinetics of Ni_3Sn_4 follow parabolic law in Ni/Sn diffusion couples in the temperature range of 235–600 °C. Consider of the $t^{1/3}$ growth kinetics, Kim and Tu [33] proposed a model which assumes that the scalloped grains coarsen by a ripening process in which the driving force is the Gibbs–Thomson effect. On the other hand, a model based on grain boundary diffusion controlling mass transport also predicts $t^{1/3}$ behavior [37]. Recently, Ghosh reported n values for Sn-3.5Ag, Sn-Bi and Sn-38Pb reacted with Ni in different temperature ranges. The n values are 4.55 at 230°C and 4.69 at 260°C for SnAg solders. Li *et. al* also reported the interfacial reactions of Ni and Ni(P) with liquid Sn-Bi solders [29]. The n value is greater than three for the thickening kinetics of Ni_3Sn_4 scallop formed in both systems. As reflected by the predicted n values here, the bulk diffusion controlled process occurred in these interfaces might only have minor effect on the thickening process and grain boundary diffusion may have a dominant effect. Differ from Ghosh and Li, we did not investigate the radial growth kinetics to get further understanding about the thickening mechanism since our samples did not allow to crosscut and observed IMC layer from top view on both EP-Ni and EL-Ni side. Therefore we mainly focused on their n values.

Indeed larger n value predicted slower reaction rate, in other words, the growth rate would reduced with time. According to our observation, the IMC shape at the EP-Ni side did not change a lot compared with IMC at the EL-Ni side. The IMC at EL-Ni side grew bigger and became layer type after more than 5 minutes reflow while the IMC at the chip side still maintained like column and faceted type. It is suggested that the growth of IMC at the EP-Ni side is only one dimension, that is, the IMC size didn't change but only changed in height. The supply of Ni atoms came form the channel between the IMC at the beginning; once the channel became IMC as well, the Ni must diffuse through IMC to react with Sn atoms. However, the Ni atoms dissolved in molten SnAg solder might react first near the column top of IMC since it was a solid-liquid interface and might easily reaction. Compare with Ni atom came from EP-Ni UBM, it needed long time to diffuse through IMC and react with Sn. It is unclear why IMC maintained the faceted shape, however it is suggested that free energy might be the main dominant factor.

III. Conclusions

Using flip-chip scale samples, the liquid-state reaction between the SnAg and the EP-Ni as well as EL-Ni has been studied at various reflowing conditions. By fabricating the EP-Ni on the chip side and the EL-Ni on the substrate side, direct comparison on the growth of Ni_3Sn_4 can be made. The IMC growth rate on the EL-Ni was faster for all the reflowing conditions. The temporal law with time exponent, n, where n is greater than three was obtained for the thickening kinetics of Ni_3Sn_4 scallops formed in both EP-Ni and EL-Ni systems. This can be attributed to that the thickening process was mainly affected by grain boundary diffusion and the radial growth reported before. During the reaction, porous Ni_3P layer, along with micro-cracks formed between the IMC and the EL-Ni layer, are observed in all conditions.

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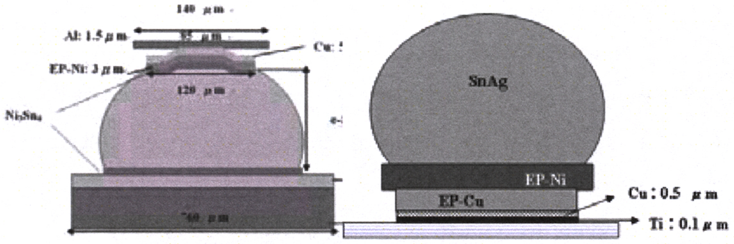
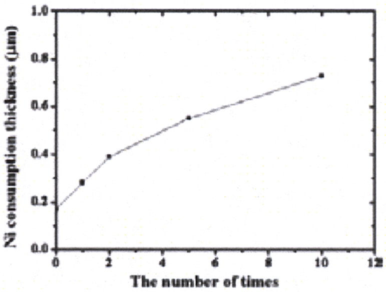
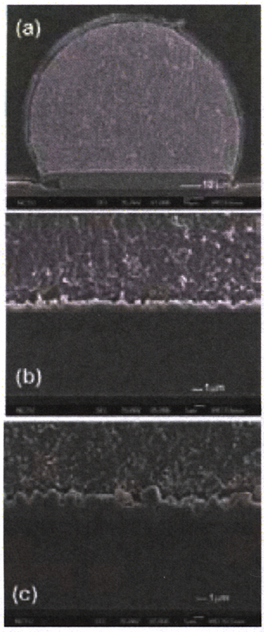
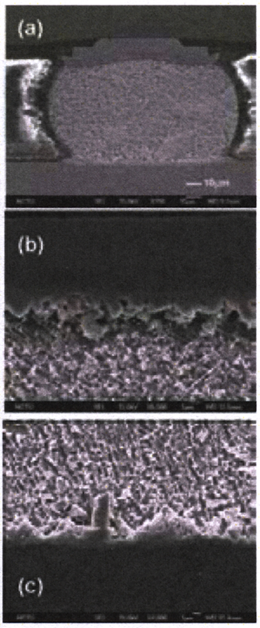
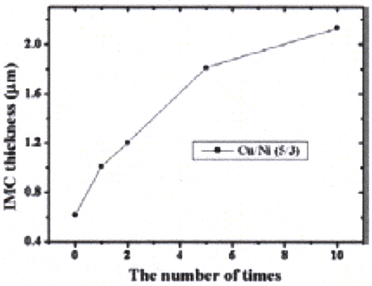
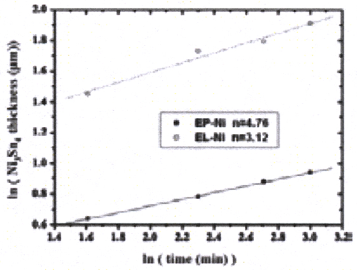

140 μm
Al: 1.5 μm
95 μm
Cu: 5
EP-Ni: 3 μm
120 μm
Ni3Sn4
760 μm
SnAg
EP-Ni
EP-Cu
Cu : 0.5 μm
Ti : 0.1 μm

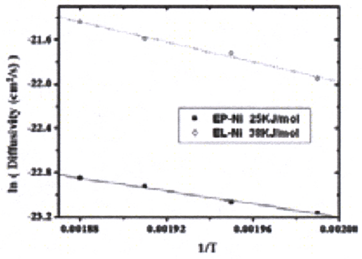

Ni consumption thickness (μm)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
The number of times

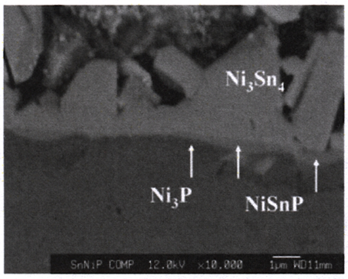

(a)
(b)
(c)


(a)
(b)
(c)


IMC thickness (μm)
2.0
1.6
1.2
0.8
0.4
0
2
4
6
8
10
Cu/Ni (5-3)
The number of times


ln (Ni3Sn4 thickness (μm))
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
EP-Ni n=4.76
EL-Ni n=3.12
ln (time (min))


ln (Diffusivity (cm²/s))
-21.6
-22.0
-22.4
-22.8
-23.2
0.00188
0.00192
0.00196
0.00200
EP-Ni 25KJ/mol
EL-Ni 38KJ/mol
1/T


Ni3Sn4
Ni3P
NiSnP