Effect of Cooling Rate on Microstructure and Strength Properties of Tin-Silver-Copper Solder Ball Bonding

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The microstructure and the strength property of Sn–3.5 mass%Ag and Sn–2.5 mass%Ag–0.8 mass%Cu solder ball bonding formed at various cooling rates were investigated. The grain size of Sn phase and the lamellar space depended on the cooling rate R_c . The reaction layer was thinner and the grain size of Sn phase coarsened when solder balls containing Cu were used. The reaction layer formed between Sn–3.5 mass%Ag and Cu pad was composed of (Ni–Au, Ag)₃Sn₄, (Ni–Au, Ag)₃Sn₂ and (Ni–Au, Ag)₃Sn precipitates. (Cu–Ni, Au, Ag)₆Sn₅ was formed in the bonding interface when the ball with Cu was used. The lamellar space in both balls became smaller at faster cooling rates and was proportional to $R_c^{(-1/2)}$. The micro Vickers hardness of the solder ball with Cu decreased slightly at the slower cooling rates because of the grain size and lamella coarsening. The shear strength of joint using Sn–2.5 mass%Ag–0.8 mass%Cu was a little higher than that using Sn–3.5 mass%Ag at the slower cooling rate because of the fine lamellar structure.

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1. Introduction

BGA technique has been applied for the high integration and reliability in the semiconductor device. The morphology of the BGA ball bonding have been researched actively since they have remarkable effects on mechanical and physical properties of the bonding.^{1,2)} In the BGA process, IC chips are set on the print board and soldered by the heat treatment in the reflow furnace. The unstable temperature and cooling rate in the furnace generates the time lag of ball solidification. So each ball structure, strength, electric property and so on are different even in the same chip. IC chips tend to incline extremely in this situation. This gives inappropriate influences directly on the durability and reliability of the semiconductor device. It is important to know the temperature distribution on the print board on which the IC devices put complexly. The index to know the best reflow condition can be gotten by surveying the solidification structure and the property of the solder balls systematically in various cooling rates. The study of the Pb free Sn alloy, for example the Sn–3.5 mass%Ag solder ball (described as 3.5Ag ball afterwards) and the Sn–2.5 mass%Ag–0.8 mass%Cu one (described as 2.5Ag–0.8Cu ball afterwards), has been performed actively for the environmental regulation.^{3–5)} Sn–Ag system balls have been investigated about the ball surface and cross section microstructure, the chemical composition and their welding property with the print board.^{6,7)} In the present study, the 3.5Ag ball and the 2.5Ag–0.8Cu one have been used as specimens. The change of Ag and Cu concentration in balls influences remarkably the mechanical properties.^{6,7)} However, systematic researches about the ball structure and the properties in various reflow conditions have not been done yet. Therefore, the 2.5Ag–0.8Cu ball, which is quite different composition compared with 3.5Ag one, has been selected as a primary study. The balls have been heated and cooled under the condition based on the reflow process. The grain size, the reaction layer thick-

ness and the morphology of intermetallic compound precipitates in the solder ball have been investigated. The mechanical property which are the hardness and the shear strength have been measured.

2. Experimental Procedure

The 3.5Ag and 2.5Ag–0.8Cu solder balls were used in this study. Both balls were supplied by Nippon Steel Co., Ltd. The Cu pads on the print boards (10 mm × 10 mm square pieces) were spread with the flux and the balls were put on the pads with tweezers. The Cu pads were covered with Ni–P electroless plating layer with about 4 μm and Au vaporize layer with about 0.1 μm. The heat treatments were accomplished in the nitrogen gas atmosphere in the furnace installed on the stage of the optical microscopy (Japan Hightech Co., Ltd.) after the specimens were put into the furnace. The temperature was raised to 513 K and hold for one minute. The temperature was measured with the thermocouple fixed to the edge of the print board piece. The melting and cooling situations were monitored with TV. When the ball on the pad melted completely, the cooling process was started. The cooling rates at 200, 100, 60, 50 and 10 K/min were performed as follows. Rates at 200 and 100 K/min were carried out by controlling the amount of nitrogen gas blowing into the furnace. Rates at 60 and 50 K/min were attained by breaking the atmosphere and controlling the amount of the air into the furnace. The rate at 10 K/min was achieved by stopping the heater. After complete solidification of the ball was confirmed in the TV monitor (at about 443 K in this study), the specimens were taken out rapidly from the furnace. SEM (accelerate voltage; 15 kV, JEOL Co., Ltd.) and optical microscopy were used for analyzing the microstructure of the ball surface and the cross section. The mixture of the nitric acid and the methyl alcohol (1:3) was used for etching. The chemical composition in the bonding cross section and the balls were surveyed with EPMA (accelerate voltage; 15 kV). The mechanical property of the balls and the bonding cross section was estimated with the micro Vickers hardness test (load; 0.05 N, time; 15 sec,

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Fig. 1 SEM micrographs of the Sn-3.5Ag ball cross section cooled at 200 K/min (a), (b) and 10 K/min (c), (d).

Fig. 2 SEM micrographs of the Sn-2.5Ag-0.8Cu ball cross section cooled at 200 K/min (a), (b) and 10 K/min (c), (d).

Shimazu Co., ltd.) and the shear test.^{8–10)}

3. Experimental Results and Considerations

3.1 Microstructure of the ball at cooling rates

Figure 1 shows the SEM micrograph of the 3.5Ag ball cross section. The microstructures of the whole area and the near surface of the ball cooled at 200 and 10 K/min are shown in Figs. 1(a), (b) and Figs. 1(c), (d), respectively. The remarkable change in the grain size of Sn phase is not seen compared with the microstructure of both cooling rates. However, the duplex structure which consists of the equiaxed grain (Sn phase) and the lamellar structure (Sn phase/Ag–Sn intermetallic compound) can be seen in Figs. 1(b) and (d). The lamellar structure was observed in the whole area. The space of the lamella becomes smaller at the faster cooling rate.

The lamellar space means the distance of Ag–Sn intermetallic compound in this study. The dependence on the cooling rate of the lamellar space has been reported before.^{11,12)} Figure 2 shows the SEM micrographs of the 2.5Ag–0.8Cu solder cross section. The microstructures of the whole area and the near surface of the 2.5Ag–0.8Cu ball cooled at 200 and 10 K/min are shown in Figs. 2(a), (b) and Fig. 2(c), (d), respectively. It is the same result that the duplex structure composed of the equiaxed grain (Sn phase) and the lamellar structure (Sn phase/Ag–Sn intermetallic compound) can be observed. There is a notable change in the grain size and the lamellar structure compared to the microstructure of balls solidified at both cooling rates. This result is different from that of 3.5Ag ball. The grain size depends on the cooling rate and that becomes smaller at the faster rate. The space of the lamella becomes smaller at the faster cooling rate compared

Fig. 3 Results of EPMA plane analysis of the Sn–3.5Ag ball cross section; SEI of the ball cooled at 200 K/min (a), 10 K/min (b) and Sn (c), Ag (d), Ni (e) and Cu (f) image of (b).

with that of 3.5Ag ball.

3.2 EPMA chemical analysis of 3.5Ag ball cross section

Figure 3 shows the result of EPMA plane analysis on the 3.5Ag ball and the Cu pad bonding cross section after cooling at 200 and 10 K/min, respectively. The reaction layer is observed in the cross section from Figs. 3(a) and (b). The white column and island-shape precipitates like the intermetallic compound grow from the interface to the ball and their length is very irregular. So complex structures are built up in the interface. The column precipitates formed by cooling at 10 K/min grow longer and bigger than that at 200 K/min. Therefore, the interface structure becomes rougher at slower cooling rate. The reaction layer with about $0.8\text{ }\mu\text{m}$ thickness was also confirmed between the Ni electroless plating layer and the column precipitates area. From Figs. 3(b) to (f), the equiaxed grain is Sn phase and lamellar structure consists of Sn phase and Ag–Sn intermetallic compound. Sn is seen in the whole area. Ni and Sn concentrate to the column precipitates. Since Ag concentrates to the gap of the column precipitates, the island-shape precipitates might be Ag–Sn intermetallic compound. There was no Au and Cu accumulation in the 3.5Ag ball and the bonding area. Au spreads rapidly and Cu diffusion from the pad to the ball was interrupted by Ni electroless plating layer. Figure 4 shows the result of EPMA line analysis on the ball and the pad bonding cross section after cooling at 10 K/min. A vertical axis expresses the composition and a transverse axis represents the analysis distance in Fig. 4(b). The length of a transverse axis is magnified the real scale of SEI (Fig. 4(a)) by about 1.5 times. Ni_3Sn_4 , Ni_3Sn_2 and Ni_3Sn might form in the interface from the Ni–Sn equilibrium state diagram.¹³⁾ From Fig. 4, Au and Ag dissolve into the intermetallic compounds. It can be considered that the column area is composed of $(\text{Ni–Au, Ag})_3\text{Sn}_4$, $(\text{Ni–Au, Ag})_3\text{Sn}_2$ and $(\text{Ni–Au, Ag})_3\text{Sn}$. However, the Ni–P intermetallic compound might precipitate in the interface or P might be contained in the Ni–Sn reaction layer as reported by Karia *et al.*¹⁴⁾

3.3 EPMA chemical analysis of 2.5Ag–0.8Cu ball cross section

Figure 5 shows the results of EPMA plane analysis on the 2.5Ag–0.8Cu ball and the Cu pad bonding cross section after cooling at 200 and 10 K/min, respectively. The reaction layer is observed in the cross section from Figs. 5(a) and (b). Though the reaction layer and the white column precipitates on the layer grow from the interface to the ball, precipitate shape is not so sharp compared with that of 3.5Ag ball. The column precipitates cooled at 10 K/min grow longer and bigger than that cooled at 200 K/min. However, the interface morphology at 10 K/min was smoother than that at 200 K/min. Since Sn is observed in the whole ball area and Ag exists in the lamellar structure, it is considered that the equiaxed grain is Sn phase and lamellar structure composed of Sn phase and Ag–Sn intermetallic compound.⁷⁾ Cu and Ag concentrate to the layer and the column precipitates. Ni distribution is not seen in the Cu diffusion area. Ni diffusion might be interrupted by the Cu diffusion area. Cu and Ag are observed between Sn phases. Since Cu and Ag are not dissolved into Sn in the Sn–Cu and Sn–Ag system equilibrium state di-

Fig. 4 Result of EPMA line analysis of the Sn–3.5Ag ball cross section cooled at 10 K/min; SEI (a), chemical compositions (b).

agram.¹³⁾ Cu and Ag were discharged to the grain boundary at 10 K/min. Figure 6 shows the result of EPMA line analysis on the ball and the pad bonding cross section after cooling at 10 K/min. Since the column precipitate in Fig. 6(a) includes 50%Sn, 10%Au, 5%Ag, 30%Cu and 5%Ni from the analyzing result of Fig. 6(b) and further Au, Ag and Ni dissolve into Cu easier than into Sn, it can be supposed from the Cu–Sn phase diagram that the precipitates is $(\text{Cu–Ag, Au, Ni})_6\text{Sn}_5$. The reaction layer, which exists between the column precipitates and Ni–P electroless plating, involves Ni and Sn mainly. So this layer might be composed of $(\text{Ni–Ag, Au, Cu})_3\text{Sn}_4$, $(\text{Ni–Ag, Au, Cu})_3\text{Sn}_2$ and $(\text{Ni–Ag, Au, Cu})_3\text{Sn}$.

3.4 The thickness of the reaction layer

Figure 7 shows the relation of the cooling rate and the thickness of the reaction layer in both balls. The layer thickness of 3.5Ag ball increases from about $1.9\text{ }\mu\text{m}$ at 200 K/min to about $4.4\text{ }\mu\text{m}$ at 10 K/min. The layer thickness in 2.5Ag–0.8Cu ball changes from approximately $1.7\text{ }\mu\text{m}$ at 200 K/min to approximately $3.6\text{ }\mu\text{m}$ at 10 K/min. The layer of 3.5Ag ball

Fig. 5 Result of EPMA plane analysis of the Sn-2.5Ag-0.8Cu ball cross section; SEI of the ball cooled at 200 K/min (a), 10 K/min (b) and Sn (c), Ag (d), Ni (e) and Cu (f) image of (b).

was very rough and the gap between the column precipitates was observed as shown in Fig. 3. Ni diffusion progressed more to the ball at the slower cooling rates and Ni distribution corresponded to the column precipitates. On the contrary, the layer of 2.5Ag-0.8Cu ball is thinner and flatter than that of 3.5Ag ball. It can be considered that the Cu-Sn reaction layer suppressed the interface reaction. Therefore, the stable Cu-Sn intermetallic compound, which can be thought as $(\text{Cu-Ag, Au, Ni})_6\text{Sn}_5$, acted as the barrier on Ni diffusion.

3.5 The structure change in the ball

Figure 8 shows the relation of the cooling rate and grain size. The grain becomes fine and the grain size of both balls is almost the same at the faster cooling rates over 50 K/min. The grain size of 3.5Ag ball changes little from approximately

8 μm at 10 K/min to approximately 13 μm at 200 K/min. It is notable that the grain size of 2.5Ag-0.8Cu ball at 10 K/min changes bigger extremely than that at the faster cooling rates. The reason might be considered as follows. No Cu and Ag dissolve into Sn in the phase diagrams and they are in saturation in the Sn phase. So Cu and Ag were discharged quickly from Sn. This might act as the driving force to the grain growth at slower cooling rates. Otherwise, the thermal conductivity from the Cu pad could influence the grain size. The conductivity from the atmosphere at the faster cooling rate is much faster than that from the Cu pad. That is because the outer temperature reduces so quickly. However, the effect of the thermal conductivity from the Cu pad could be more remarkable than that from the atmosphere at the slower cooling rate. The Cu-Sn reaction layer might act as the ther-

Fig. 6 Result of EPMA line analysis of the Sn-2.5Ag-0.8Cu ball cross section cooled at 10 K/min; SEI (a), chemical compositions (b).

Fig. 7 Relation of cooling rate and thickness of reaction layer.

mal barrier. Therefore, it can be supposed that the grain size might become bigger and more different from the interface

Fig. 8 Relation of cooling rate and grain size.

Fig. 9 Relation of cooling rate and lamellar space observed in Sn-3.5Ag and Sn-2.5Ag-0.8Cu ball.

Fig. 10 Relation of cooling rate and micro Vickers hardness.

and surface. The detail about this phenomenon is under study. Figure 9 shows the relation of $Rc^{(-1/2)}$ and lamellar space λ . The measure of the lamellar space was carried out as follows. The minimum lamellar space in the whole ball area was ob-

Fig. 11 Relation of cooling rate and shear stress.

Fig. 12 SEM micrographs of the Sn-2.5Ag-0.8Cu ball cross section cooled at 10 K/min after the shear test; ball side (a) and pad side (b).

served with SEM and calculated by comparing with the scale of SEM micrographs. There is the relation of R_c and λ as follows.^{15,16)}

$$\lambda = C_0 \cdot R_c^{(-1/2)} \quad (1)$$

Where both ball's C_0 values are constant and they are 7 and 5.5, respectively. The lamellar space of 2.5Ag-0.8Cu ball is smaller than that of 3.5Ag one at the cooling rates. It is apparent from Fig. 6 that Cu dissolves into Ag of Ag-Sn intermetallic compound. But the maximum solution of Cu into Ag is about 0.35 mass%. Therefore, Cu might contribute to

Fig. 13 SEM micrographs of the Sn-2.5Ag-0.8Cu ball side cooled at 10 K/min after the shear test.

the smaller lamellar space by the precipitates in the lamellar interface of Sn phase and Ag-Sn intermetallic compound.

3.6 Strength property of the ball and cross section

Figure 10 shows the relation of the cooling rate and the micro Vickers hardness. There was no deflection of the hardness value in the ball area. The hardness value of 3.5Ag ball is constant through the cooling rate. The hardness value of 2.5Ag-0.8Cu ball decreases slightly at the slower cooling rate. The grain and the lamella coarsen especially at 10 K/min influence the hardness descent. Figure 11 shows the relation of the cooling rate and the shear strength. The value was the average one of twenty measures. The strength of each ball is almost the same at the rates. The shear strength of 2.5Ag-0.8Cu ball is little bigger than that of 3.5Ag ball at the rates. Figure 12 shows SEM micrographs of the fracture face on the both 2.5Ag-0.8Cu ball and the pad sides after the shear test. Though the specimen was not the same, this fracture morphology as shown in Fig. 12 was typical one in both balls. The fracture occurred in the ball side not in the interface. So the shear failure probably started in the edge of the neck part. Figure 13 shows SEM micrograph magnified Fig. 12(a). There is some fractured Ag-Sn precipitates (arrows in Fig. 13), which is a part of the lamellar structure, in the dimples. The dimple area corresponds to the ductile Sn phase. It can be thought that Ag-Sn precipitates in the lamella, which space is smaller than that of 3.5Ag ball as shown in Fig. 9, influenced the shear strength more than Sn phase.

4. Conclusions

The microstructure and the strength property of Sn-3.5Ag and Sn-2.5Ag-0.8Cu solder ball on the Cu pad at different cooling rates ($R_c = 10 \sim 200$ K/min) have been investigated. The results in the present study are described as follows.

(1) The grain size and the lamellar space of both balls depended on the cooling rate and became bigger at the slower cooling rate.

(2) In 3.5Ag ball, the reaction layer consisted of the (Ni–Ag, Cu)–Sn and Ag–Sn intermetallic compounds. The reaction layer consisted of the (Cu–Ag, Au, Ni)–Sn and (Ni–Ag, Cu)–Sn intermetallic compounds in 2.5Ag–0.8Cu ball.

(3) Sn and Ag–Sn lamellar space of 2.5Ag–0.8Cu ball was smaller than that of 3.5Ag ball and was proportional to $R_c^{(-1/2)}$.

(4) The micro Vickers hardness of 2.5Ag–0.8Cu ball decreased slightly at the slower cooling rate. That was because the grain and lamella coarsened.

(5) The fracture occurred at the neck part of the ball. The shear strength of 2.5Ag–0.8Cu was a little bigger than that of 3.5Ag ball. That might be due to the fine lamellar structure.

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