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Formation of nearly void-free Cu_3Sn intermetallic joints using nanotwinned Cu metallization

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Cu_3Sn intermetallic compounds (IMCs) are more resistant to fracture than solders. In addition, the Cu_3Sn IMCs are more conductive than the solders. In this study, we manufactured Cu_3Sn IMCs to serve as a joint using electroplated nanotwinned Cu as a metallization layer to react with pure Sn at 260 °C and 340 °C. The results show that there were almost no Kirkendall voids generated inside the Cu_3Sn layer. In addition, the kinetics of the Cu_3Sn growth was analyzed to predict the time needed to form the Cu_3Sn joint. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4874608]

A 3D integrated circuit (3D IC) is a stack of different chips that performs vertical integration in a 3D space. Microbumps made of copper-tin are typically used as joints between chips because copper-tin is better than copper-nickel in terms of wetting.[1,2] The copper-tin system metallurgical reaction has been well studied over the years. It involves the formation of two types of intermetallic compounds (IMCs): Cu_6Sn_5 and Cu_3Sn.[3–6] The Cu-Sn intermetallic compound has become very important for electronics packaging.[7–11] Other studies have focused on the properties of the Cu-Sn intermetallic compounds. Cu_6Sn_5 and Cu_3Sn have relatively good mechanical properties. They are better than Sn in terms of melting temperature, Young's modulus and hardness.[12–16] In addition, the Cu_3Sn fracture toughness is 5.72 MPa/m$^{1/2}$, which is double the value for Cu_6Sn_5 (2.80 MPa/m$^{1/2}$). By comparing the two types of IMCs, it has been shown that Cu_3Sn is better at resisting fracture.[14] The electrical resistivity of Cu_3Sn of 8.9 $\mu\Omega\cdot$cm is lower than that of the Sn of 11.5 $\mu\Omega\cdot$cm and Cu_6Sn_5 of 17.5 $\mu\Omega\cdot$cm. In addition, the elastic modulus of Sn, Cu_6Sn_5, and Cu_3Sn are 26.2, 85.56, and 108.3 MPa, respectively.[15] Because of its mechanical properties, Cu_3Sn is also more suitable than Cu_6Sn_5 and Sn as a joint material for microbumps. Because there is a need for more I/O components in electronic components, more I/O components must be manufactured within the same area. As the switching component density increases inside the chip, the flip-chip joint diameter must shrink. In a 100 μm diameter flip-chip joint, the solder volume is significantly larger than the under bump metallization (UBM) volume. Nevertheless, as the solder diameter is reduced from 100 μm to 20μm, the solder volume is reduced approximately by 1/125. Under that condition, the volume of the UBM in the microbump becomes larger than the solder volume. As a result, the solder may be converted to intermetallic compounds. Therefore, the properties of the intermetallic compounds become critical for reliability issues. Using intermetallic compounds with good properties, Li *et al.* have tried to use 25 μm-thick Sn foil and two pieces of 10 μm-thick Cu foils to form sandwich structures by reflow to form a Cu_3Sn layer thickness of under 10 μm without generating any Kirkendall voids.[17] Cu_3Sn layers can also be generated using aging with a solder layer (less than 1 μm) and a Cu UBM. Furthermore, Li *et al.* used ultrasonic bonding process at ambient temperatures to form full Cu/Cu_3Sn/Cu joint in 14 s; however, numerous microvoids formed in the Cu_3Sn layer.[18]

If the temperature is too high or the duration is too long for forming the Cu_3Sn microbumps, the use of Cu and Sn foils for manufacturing will not be suitable for electronics packaging. For electronics packaging, electroplated copper is used for the UBM and wires. Cu_3Sn formed by metallurgical reactions using electroplated copper and tin can generate Kirkendall voids, which endanger the reliabilities of the microelectronics devices.[19–22]

Hsiao *et al.* adopted densely packed [111] nanotwinned Cu (nt-Cu) for UBM, with a thickness of 20 μm.[23] When aged at 150 °C, the Sn3.5Ag reacted with the nt-Cu to form intermetallic joints with the Cu_6Sn_5 and Cu_3Sn IMCs. No voids are generated during this metallurgical reaction.

In the present work, we use nt-Cu for UBM to react with pure Sn in molten state. By selecting 260 °C and 340 °C as reflowing temperatures and changing the solder height for reflowing, we investigate the time required to form complete Cu_3Sn joints and the status of the generation of voids in the joints. Microbumps made of Cu_3Sn IMCs are formed after Sn is completely consumed. By controlling the Sn height, Cu_3Sn joints are formed in short periods of time at a reflowing temperature of 260 °C. This process does not generate voids in the Cu_3Sn layer, and the nt-Cu columnar grains are maintained.

We used electroplating of nt-Cu columnar grain structures to manufacture nt-Cu/Sn/nt-Cu and regular copper electroplating to manufacture the Cu/Sn/Cu structure. The manufactured nt-Cu specimen can be divided into the pad and the film. A 20 nm layer of Cu was sputtered onto a Si wafer with a 100-nm-thick Ti layer. The Cu was used as a seed layer. The pad manufacturing process included an exposure and a development process. After the pattern was defined, the nt-Cu was electroplated onto it. The procedure for the nt-Cu electroplating has been reported previously.[23] The electroplated nt-Cu pad was circular, with a diameter of 100 μm and a thickness of 20 μm. The nt-Cu film was 10 μm thick, whereas the regular electroplated Cu film was 60 μm thick. When the tin was electroplated on the copper

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substrates at room temperature, the thickness of the electroplated-tin layer on the nt-Cu pad was 0.44 μm. The electroplating-tin-layer thickness on the nt-Cu film was 1 μm. The tin-layer thickness on the regular Cu film was 60 μm. For joining the tin electroplated substrates and the copper electroplated substrate, we applied flux on the Sn layer and reflowed the samples at 260 °C for 1 min. We then applied pressures of 9.6 MPa and 0.78 MPa to the 0.44 μm bumps and 1 μm films, respectively. After a 1-min reflow, the pad-to-pad and film-to-film microbumps were formed. We manufactured 0.44, 1, and 10 μm-thick Sn layer between nt-Cu UBMs and a 60 μm-thick Sn layer between regular Cu UBMs. For the flip-chip microbumps associated with the 60 μm -thick layers, the reflow lasted for 24 h at 340 °C. For the flip chip microbumps associated with the 10 μm-thick layers, the reflow lasted for 20, 60 min, or 24 h at 260 °C or for 5, 40, or 60 min at 340 °C. For the flip chip microbumps associated with the 1 μm-thick layers, the reflow lasted for 10 min at 260 °C with 0.78 MPa added pressure. For the flip chip microbumps associated with the 0.44 μm -thick layers, the reflow lasted for 3 min at 260 °C with a pressure of 9.60 MPa. All of the samples went through the reflow process under normal atmospheric conditions. Table I summarizes the structures and experimental conditions for the samples in this study. After the reflow, the samples underwent grinding and polishing using alumina powder to reveal their microstructures. Scanning electron microscopy (SEM) was used to observe microstructural changes. A focused ion beam (FIB) was used to grind and polish the cross sections to observe the Kirkenall voids.

When using the regular Cu film without nanotwinned columnar grains and the liquid-state Sn film for the reflow reaction, Kirkendall voids were observed in the Cu_3Sn layer close to the original interface of Cu_3Sn and Cu. Figure 1 shows these microstructures in an SEM cross-section after the metallurgical reaction at 340 °C for 24 h. Th original Sn thickness was 60 μm. Regular electroplated Cu was used as the UBM materials. In the metallurgical reaction, the tin layer was almost consumed such that a 100-μm-thick Cu_3Sn layer was formed. Many Kirkendall voids were generated in the Cu_3Sn layer, which is consistent with previous reports.[19–22] The Kirkendall voids may weaken the mechanical properties of the Cu_3Sn IMC joint. We tried to eliminate the Kirkendall voids by adopting the nt-Cu as the UBM materials for the reflow reaction. By using nt-Cu, almost void-free Cu_3Sn joints can be manufactured. Figure 2(a) shows the initial state of the nt-Cu/Sn/nt-Cu with a solder thickness of 10 μm at 260 °C after 1 min of soldering. The

TABLE I. Structures and experimental conditions for the test samples of Cu/Sn/Cu and nt-Cu/Sn/nt-Cu.

Sample	Sn thickness	Applied pressure	Reflow temperature	Reflow time
Cu/Sn/Cu	60 μm	No	340 °C	24 h
nt-Cu/Sn/nt-Cu	10 μm	None	340 °C	1, 5, 40, 60 min
	10 μm	None	260 °C	1, 20, 60 min, 24 h
	1 μm	0.78 MPa	260 °C	10 min
	0.44 μm	9.60 MPa	260 °C	3 min

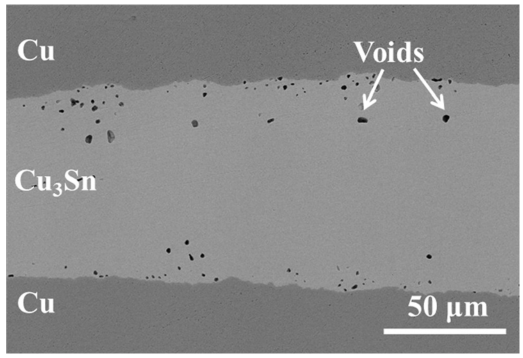

FIG. 1. SEM image taken from the polished cross-section of $Cu/Cu_3Sn/Cu$ without nanotwinned Cu. Many voids were found at the Cu/Cu_3Sn interface.

tin was the main part of the joint. The thickness of the scallop-type Cu_6Sn_5 was approximately 2 μm. Figure 2(b) shows the state after continuous reflow at 260 °C for 20 min. The tin was gradually consumed to produce Cu_6Sn_5 and Cu_3Sn IMCs. The Cu_6Sn_5 IMCs on both sides were connected to each other. In addition, a 1-μm-thick l Cu_3Sn was formed after continuous reflowing for 60 min between the Cu_6Sn_5 and the Cu. As shown in Figure 2(c), the tin was completely consumed, and the Cu_6Sn_5 was connected to a single layer. Layers of 2.30-μm-thick and 2.87-μm-thick Cu_3Sn were formed at the top and the bottom side, respectively. Finally, after reflow for 24 h, the Cu_6Sn_5 was converted to Cu_3Sn to form a pure Cu_3Sn joint. At the interface of the Cu_3Sn layer and the Cu, almost no Kirkendall voids were generated, as shown in Figure 2(d).

When the reflowing temperature increased, the metallurgical reaction speed increased such that the time needed to

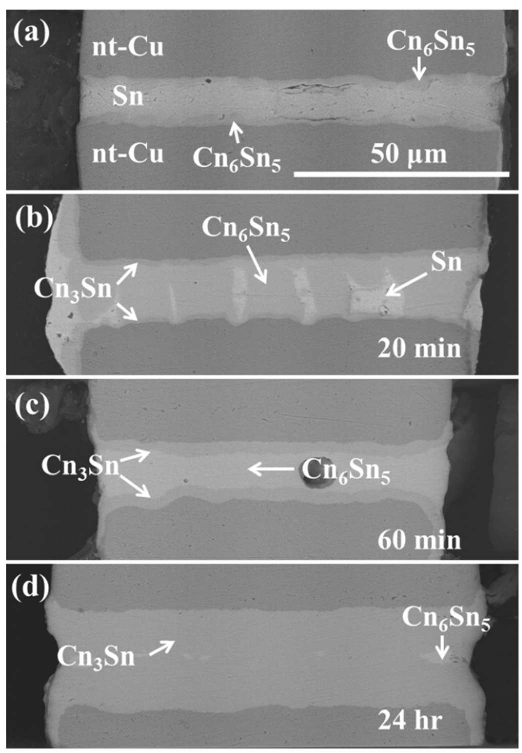

FIG. 2. SEM images taken from the polished cross-section of nt-Cu/Sn/nt-Cu sample reflowed at 260 °C for: (a) as-reflowed; (b) 20 min; (c) 60 min; and (d) 24 h.

form the Cu_3Sn IMC was reduced. Figure 3(a) shows the initial state of the nt-Cu/Sn/nt-Cu at 260 °C after 1 min of reflow for a 10 μm -thick solder. After 5 min of reflow at 340 °C, the tin was completely consumed, with a layer of Cu_6Sn_5 formed at the both sides of the joint. The Cu_6Sn_5 IMCs became the main part of the solder, producing 2.34 and 2.90 μm-thick layers of Cu_3Sn at the top and the bottom sides, respectively, as shown in Figure 3(b). After 40 min of reflow, the metallurgical reaction consumed the Cu_6Sn_5 IMCs, while the Cu_3Sn continued to grow. Cu_3Sn layers of 7.76 μm and 6.92 μm were generated at the top and the bottom sides of the joint, respectively, as shown in Figure 3(c). Finally, after 1 h of reflow, the Cu_3Sn layers at the both sides started to make contact. The Cu_3Sn then became the main part of the solder as the connection was formed. Almost no Kirkendall voids were observed at the interfaces between the Cu_3Sn layer and Cu, as shown in Figure 3(d). For a tin thickness of 10 μm, a 23 μm-thick Cu_3Sn layer was formed by reflowing at 260 °C. Increasing the temperature reduced the thickness of the Cu_3Sn layer formed during the reflow.

By reducing the Sn thickness, we were able to lower the reflow temperature to 260 °C to form a complete Cu_3Sn joint. We were also able to reduce the time needed for the process. As shown in Figure 4(a), using a solder thickness of 1 μm at 260 °C and a reflow time of 10 min, we were able to form a 2.7-μm-thick Cu_3Sn joint with almost all of the Cu_6Sn_5 consumed. No voids were produced in the Cu_3Sn layer. To affirm the void distribution, we used a FIB to polish the surface of the Cu_3Sn layer, as shown in Figure 4(b). Almost no Kirkendall voids were produced in the Cu_3Sn layer. Therefore, lowering the Sn thickness can effectively reduce the reflow time needed to form a Cu_3Sn joint.

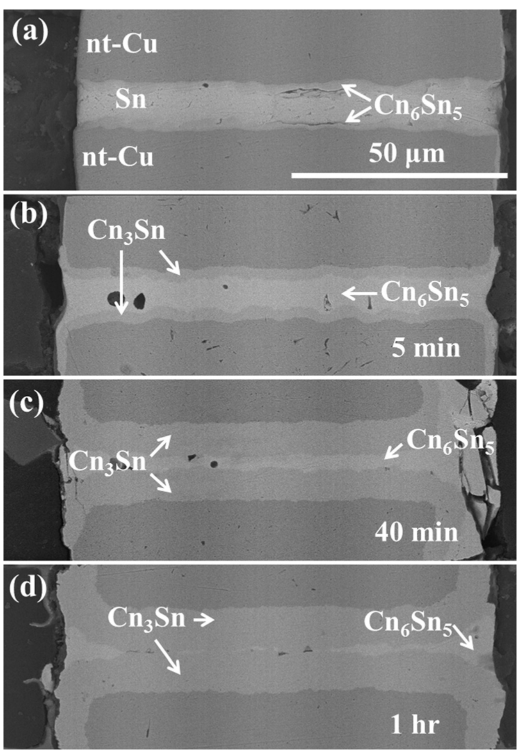

FIG. 3. SEM images taken from the polished cross-section of the nt-Cu/Sn/nt-Cu sample reflowed at 340 °C for (a) as-reflowed; (b) 5 min; (c) 40 min; and (d) 1 h.

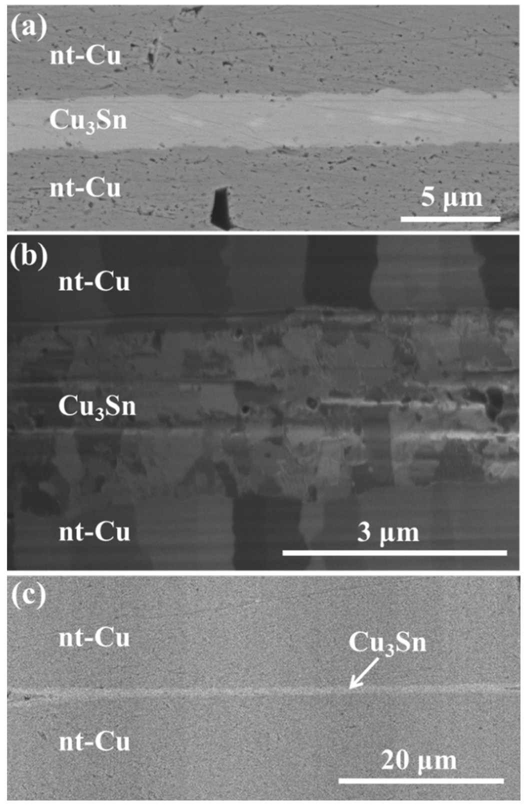

FIG. 4. (a) SEM and (b) FIB images of the nt-Cu/Cu_3Sn/nt-Cu sample after the reflow at 260 °C for 10 min. (c) SEM image of the nt-Cu/ Cu_3Sn/nt-Cu sample reflowed at 260 °C for 3 min.

We also continued to lower the solder amount. As shown in Figure 4(c), for a 0.44-μm-thick Sn layer formed by a 3-min reflow at 260 °C, a 1 μm-thick Cu_3Sn joint was formed without any voids. Therefore, we can use our electroplating method to electroplate nt-Cu to control the solder thickness and the reflow time needed for the solder to form nearly void-free Cu_3Sn IMC joints.

The nt-Cu is able to eliminate Kirkendall voids because of the following two reasons. First, the nt-Cu has less residual sulfur impurities after electroplating. It is reported that sulfur atoms in Cu may cause Kirkendall voids in Cu/Sn reactions.[24–26] When electroplating Cu films, the sulfur atoms in the electroplating solution can precipitate out and become incorporated into the grain boundaries.[25] In contrast, the nt-Cu columnar grains can effectively reduce the area of grain boundary per unit volume and further reduce the sulfur impurities left in the Cu films. Therefore, nt-Cu can effectively reduce the generation of Kirkendall voids. Second, the densely packed nanotwins in Cu may serve as vacancy sinks. Several researchers reported that there are many defects, such as steps and kinks in Cu nanotwins.[27–29] These defects are all vacancy sinks; therefore, the vacancy concentration is effectively reduced, such that the concentration does not exceed the saturation concentration required to nucleate the voids.

The kinetics of the Cu_3Sn growth was also analyzed below. For the microbumps with solder thicknesses of 10 μm, it took 24 h at 260 °C to form Cu_3Sn joints, whereas it took 1 h at 340 °C to grow Cu_3Sn joints. Higher temperatures can increase the IMC growth velocity. It is known that the scallop-shaped Cu_6Sn_5 grows under ripening control, while the layered Cu_3Sn grows under diffusion control.[17] We used the Arrhenius equation[30] and the kinetic growth equation to estimate the time for converting the Sn to Cu_3Sn IMCs, as follows:

$$k^2(T) = k_0^2 \exp\left(-\frac{E_a}{RT}\right), \tag{1}$$

$$x(t) = kt^{0.5}. \tag{2}$$

The term k denotes the growth rate constant, while k_0 is the frequency factor, E_a is the activation energy, T is the absolute temperature, R (=8.314 J/mol·K) is the gas constant and x and t are the Sn thickness and time needed to form Cu_3Sn, respectively. We combined Eqs. (1) and (2) to obtain the following equation:

$$x(t,T) = k_0^{0.5} \exp\left(-\frac{E_a}{2RT}\right) t^{0.5}. \tag{3}$$

Equation (3) shows that a temperature increase can exponentially reduce the reflow time. At a fixed temperature, the thickness is proportional to the square root of the reflow time. In our experiment, the temperature increase was used to reduce the reflow time. There was still no generation of Kirkendall voids in the Cu_3Sn layer. However, high reflow temperatures can lead to the damage of electronic components. Therefore, we chose to change the solder height such that the reflow temperature could be reduced to 260 °C, as shown in Figure 4. After lowering the solder heights to either 1 or 0.44 μm, Cu_3Sn joints were formed after either 10 or 3 min. Based on the time needed to form the pure Cu_3Sn layers for these three solder heights at 260 °C, we obtain

$$x(t) = 0.0338\, t^{0.5} + 0.0078, \tag{4}$$

where x(t) is in microns and t is in seconds. The derived n = 0.5 value shows that the Sn reaction to form Cu_3Sn is occurs under diffusion control. We can use Eq. (4) to estimate the reflow time or solder thickness. For example, we need a 1 min reflow at 260 °C to form a Cu_3Sn joint. After using the formula, we can derive the thickness needed for electroplating, which is 0.27 μm. The melting point of the Cu_3Sn IMC is as high as 676 °C.[15] Its Young's modulus is also higher than that of Pb-free solders. Thus, the Cu_3Sn joints are expected to have better electromigration resistance.[31,32] In addition, the fracture toughness of Cu_3Sn is higher than those of Cu_6Sn_5 and Pb-free solders. The mechanical properties of Cu_3Sn are also better than those of Cu_6Sn_5.[33] Therefore, the Cu_3Sn joints may have great potential as interconnects in 3D ICs.

In summary, using nt-Cu as the metallization films, we can fabricate Cu_3Sn IMC joint almost without Kirkendall voids. At 260 °C, the reflow converted the entire molten-state of Sn and Cu_6Sn_5 into a Cu_3Sn joint while maintaining the nt-Cu columnar grain structure. We demonstrated that we can lower the temperature for the formation of the Cu_3Sn joint to 260 °C with duration of several minutes. In addition, using kinetics analysis, we can forecast the time needed for Sn to form Cu_3Sn joints at 260 °C. These Cu_3Sn microbumps are expected to possess better electromigration resistance and mechanical properties. The fabrication of void-free Cu_3Sn joints has great potential to be applied to 3D integrated circuit microbumps and other joints.

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