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ARTICLE

Effect of Ni Addition in Sn0.7Ag0.5Cu on Interfacial Reaction and IMC Growth of Cu and Graphene-coated Cu Substrates

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Abstract: The formation and growth of intermetallic compound (IMC) layer at the interface between Sn0.7Ag0.5Cu (SAC0705) solder and Cu or graphene-coated Cu (G-Cu) substrates were investigated during soldering and aging. The samples were soldered on a heating platform by aging treatment at 120 ℃ for up to 600 h. The results show that the thickness of IMC increases with increasing the aging time. The Cu_6Sn_5 IMC layer is observed at SAC0705/Cu and SAC0705/G-Cu interfaces. With the addition of Ni element in the solder, Cu_6Sn_5 transforms into $(Cu, Ni)_6Sn_5$. With the increase of Ni content, the thickness of IMC shows an increase trend first and then decreases on the two kinds of substrates. Moreover, as the Ni content increases, the growth rate constant of interfacial IMC layer decreases. Since the graphene layer works as a diffusion barrier, the IMC on G-Cu is thinner than that on Cu substrate. And the growth rate constant of the interfacial IMC on G-Cu substrate is lower than that on Cu substrate.

Key words: graphene-coated Cu; solder joints; intermetallic compound; Ni element

In recent years, Pb-free solders have been greatly developed. Due to low melting temperature, good solderability and mechanical properties, Sn-Ag-Cu solder is widely used in the interconnection of microelectronic devices[1,2]. However, several problems of using SAC solder have appeared, such as excessive growth of IMC, microvoid formation at the interface between Cu substrate and solder, and high undercooling during solidification. These problems influence the reliability of solder joints. Therefore, many researchers add a small amount of different types of alloying elements into lead-free solder alloys to enhance the reliability of solder joints. Tao et al[3] studied the effects of Ni and Sb addition on mechanical properties and microstructure of lead-free solder joints. They found that the addition of Ni and Sb element can lead to the formation of new $(Cu, Ni)_6Sn_5$ and $Ag_3(Sn, Sb)$ during the interfacial reaction between solder and Cu substrate. Besides, Li et al[4] observed the effect of aging temperature and Ni addition on the interfacial IMC layer and tensile properties of Sn0.7Cu solder joint. In their experiment, brittle Cu_3Sn layer was observed between Cu_6Sn_5 layer and Cu substrate in Cu/Sn0.7Cu/Cu joints after aging at 60 ℃, while $(Cu, Ni)_3Sn$ IMC layer was detected after aging at 140 ℃ in Cu/Sn0.7Cu-0.05Ni/Cu. Compared with Cu/Sn0.7Cu/Cu joint, the interfacial morphology directly changed from scallop-shaped into layer-shaped structure with lower Gibbs free energy. So, the layer thickness is obviously suppressed after adding of Ni particle.

Furthermore, it has been reported that the treated Cu substrate can also inhibit the growth of IMC layer at the in-

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terface of solder joints. Zhang et al[5] investigated the effect of Ni addition to Cu substrate on the interfacial reaction and IMC growth with Sn3.0Ag0.5Cu solder, and they found that the growth of IMC can be effectively suppressed. Besides, the study of Gao et al[6] indicated that the addition of 1 at% *X* (*X*=Mn, Ni or Ag) to Cu substrate decreases the total thickness of the IMCs after annealing at 423 K. Moreover, Chen et al[7] used chemical vapor deposition (CVD) to prepare graphene layers on the surface of Cu and Cu/Ni substrates. The graphene layer worked as a barrier to oxygen molecules at 200 ℃. It effectively suppressed the surface oxidation of Cu and Cu/Ni substrates. If the graphene-coated Cu (G-Cu) is used as soldering substrate, it is expected that the graphene layer hinders the interfacial diffusion and suppresses the coarsening of the interfacial IMC in the solder joint.

Although great efforts have been made to study the interfacial reactions of SAC0705 solder on Cu substrates. The research on the interfacial reaction and the growth of IMC between SAC0705-*x*Ni and G-Cu substrate is still scarce. Consequently, this paper focused on the effect of Ni addition in Sn0.7Ag0.5Cu on the interfacial reaction and IMC growth of Cu substrate and grapheme-coated Cu substrate.

1 Experiment

The preparation method of graphene-coated Cu (G-Cu) substrates is as follows:

Cu substrate was heated to 1000 ℃ in a heating furnace with the gas of Ar (300 mL/min) and H_2 (50 mL/min) for 30 min. Then the gas of CH_4 (5 mL/min), Ar (500 mL/min) and H_2 (50 mL/min) was passed into the furnace at 1000 ℃ for 8 min. At the end, the pads were cooled in a furnace with the protective gas of Ar (300 mL/min) and H_2 (50 mL/min).

Meanwhile, the Raman curve in Fig.1 approves that graphene layer is successfully coated on the G-Cu substrate.

SAC0705-*x*Ni alloys (*x*=0, 0.05, 0.3, wt%) were prepared as solder by melting pure Sn, Ag, Cu and Ni together in a induction-furnace according to their mass percentage. The solder alloys were made into solder balls with 0.02 g in mass and 1.75 mm in diameter. Then the solder balls were placed on Cu and G-Cu substrates with flux. The samples were soldered on a heating platform. The soldering temperature was 260 ℃ and the soldering time was 60 s. The soldered samples were aged isothermally at 120 ℃ in the oven for 0, 100, 300 and 600 h. The samples were polished and etched for cross-sectional observation. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDS) analysis were used to investigate the microstructure and constituent of solder joints.

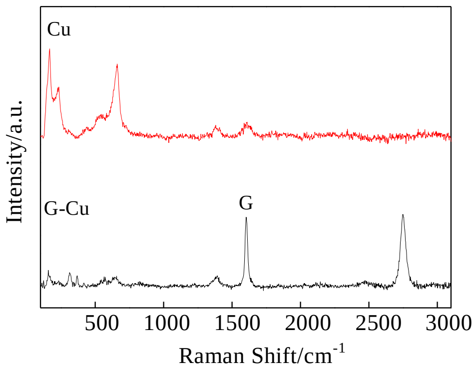

Fig.1 Raman curves of the graphene-coated Cu substrates

The equivalent thickness of the IMCs was measured by the SEM image of the metallographic cross-sections. Then, the equivalent thickness (L_{IMC}) of the individual layer was calculated using the following equation:

$$L_{IMC} = H_{IMC}/H_{SEM} \cdot L_{SEM} \quad (1)$$

where L_{IMC} is actual height of the individual SEM image, and H_{IMC} and H_{SEM} are numbers of pixels in the IMC layers and entire SEM image, respectively.

2 Results and Discussion

Fig.2 shows the interfacial cross-section images of SAC0705/Cu solder aged at 120 ℃ for 0, 100, 600 h and EDS analysis of SAC0705/Cu interface aged at 120 ℃ for 600 h. After soldering, only the scallop-type Cu_6Sn_5 IMC forms at the interface of SAC0705/Cu solder joints, as shown in Fig.1a. Moreover, it is clearly found that the Cu_6Sn_5 IMC layer tends to change from the scallop-type to planar-type with prolonging the aging time, as shown in Fig.2a~2c. The reason why the IMC growth at the valleys between two adjacent scallops is faster than at the peaks of the scallops during the solid-state aging was reported by Lee et al[8]. As shown in Fig.2, there is Cu_6Sn_5 IMC in the solder bulk. Intermetallic compound (IMC) phases formed at the interface of SAC0705/Cu solder joints are obviously identified by EDS, as shown in Fig.2d. According to spectrum results, the atomic percent of Cu element is 48.53 at% and the Sn content is 51.47 at%. Then, the ratio of Cu to Sn approaches 6 to 5, so it can be identified as Cu_6Sn_5 phase.

Fig.3 presents the SEM images of SAC0705/G-Cu solder joints after soldering and isothermal aging treatment for different time and EDS analysis of SAC0705/Cu interface aged at 120 ℃ for 600 h. The Cu_6Sn_5 IMC is also observed at the interface of SAC0705 and G-Cu substrates, as shown in Fig.3a. Besides, there is Cu_6Sn_5 IMC in the solder bulk. The isothermal aging treatment has similar effects on the solder bulks on Cu and G-Cu substrate. Meanwhile, the EDS analysis of SAC0705/G-Cu interface aged at 120 ℃ for 600 h is shown in Fig.3d. It evidently shows that the IMC at the interface is Cu_6Sn_5.

The cross-sectional SEM images of SAC0705-*x*Ni/Cu (*x*=0.05, 0.3, wt%) solder joints are shown in Fig.4. There are the continuous phases of scallop-like Cu_6Sn_5 at the interfaces of SAC0705-*x*Ni/Cu system. Due to the addition of

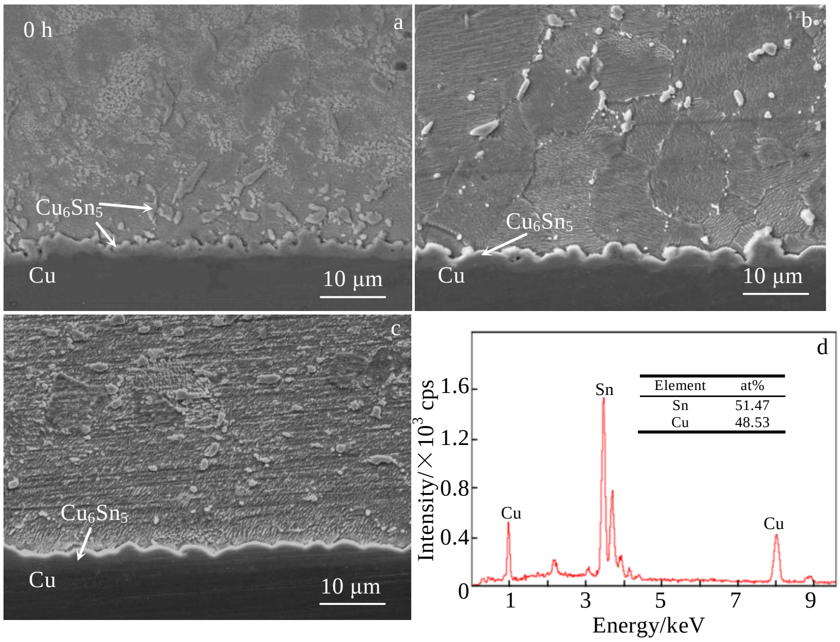

Fig.2 SEM images of interfacial microstructure of SAC0705/Cu interface after soldering and isothermal aging at 120 ℃ for different time: (a) 0 h, soldering state, (b) 100 h, and (c) 600 h; EDS spectrum of Cu_6Sn_5 in Fig.2c (d)

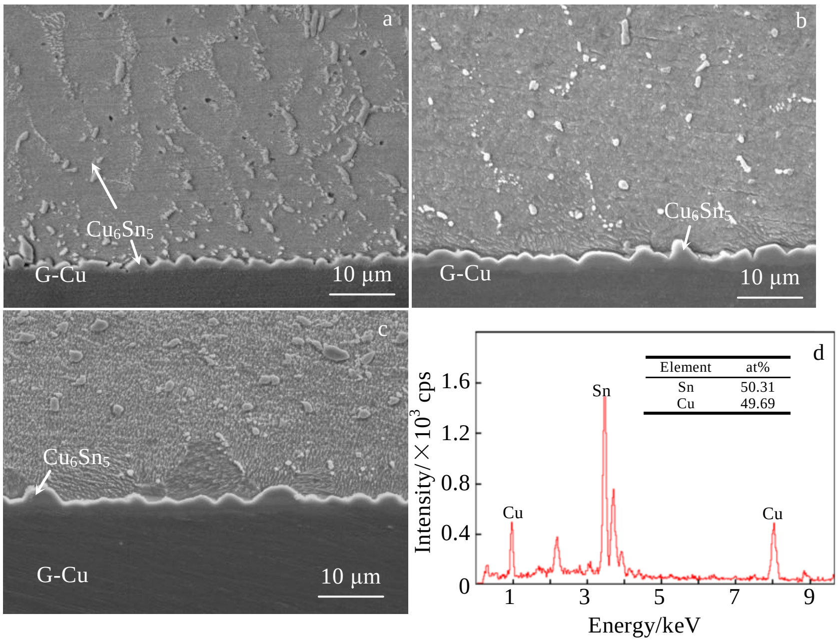

Fig.3 SEM images showing the interfacial microstructure of the SAC0705/G-Cu interface after soldering and isothermal aging at 120 ℃ for different time: (a) 0 h, soldering state, (b) 100 h, and (c) 600 h; EDS spectrum of Cu_6Sn_5 in Fig.3c (d)

Ni element, the new IMC layer forms at the interface of SAC0705-*x*Ni/Cu solder joints. With the addition of Ni, it is (Cu, Ni)$_6$Sn$_5$ instead of Cu_6Sn_5 at interface, as shown in Fig.4a. With the addition of Ni in SAC0705, Cu_6Sn_5 becomes (Cu, Ni)$_6$Sn$_5$ in the solder bulk in Fig.4. And as the Ni content increases in SAC0705-*x*Ni, the (Cu, Ni)$_6$Sn$_5$ IMC layer shows a smooth surface. Fig.5a is amplification of selected area in Fig.4d. Fig.5b shows the EDS result of SAC0705-0.3Ni/Cu aged for 600 h in Fig.5a. The composition of 39.46 at% Sn, 2.56 at% Ni and 57.98 at% Cu is presented in Fig.5b, which is identified as (Cu, Ni)$_6$Sn$_5$ phase.

Fig.6 demonstrates the cross-sectional SEM images of the solder joint interfaces between the SAC0705-*x*Ni solder and G-Cu substrate soldered at 260 ℃ for 1 min and aged

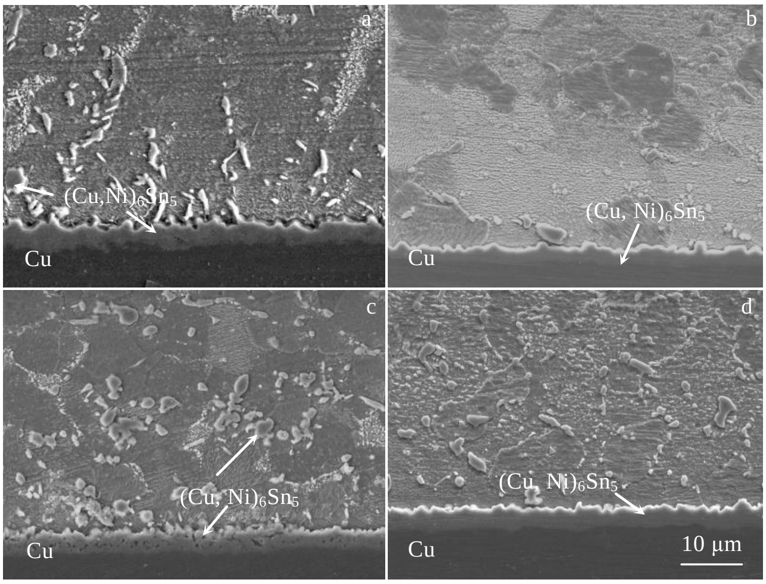

Fig.4 SEM images of the interfacial microstructure of SAC0705-*x*Ni/Cu interface after soldering and isothermal aging at 120 ℃ for 0 h (a, c) and 600 h (a, b): SAC0705-0.05Ni and (c, d) SAC0705-0.3Ni

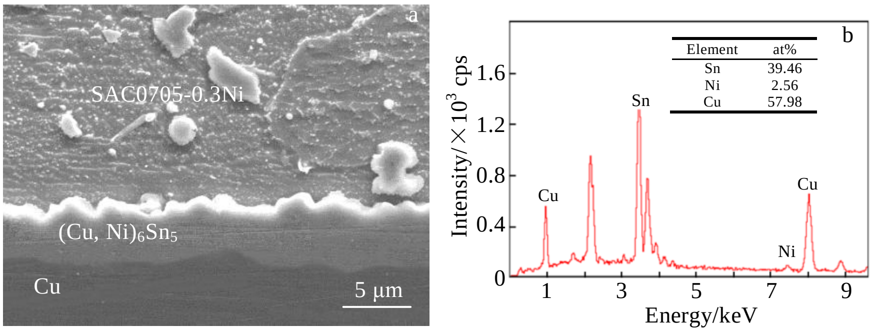

Fig.5 SEM image (a) and EDS spectrum (b) of SAC0705-0.3Ni/Cu interface aged at 120 ℃ for 600 h

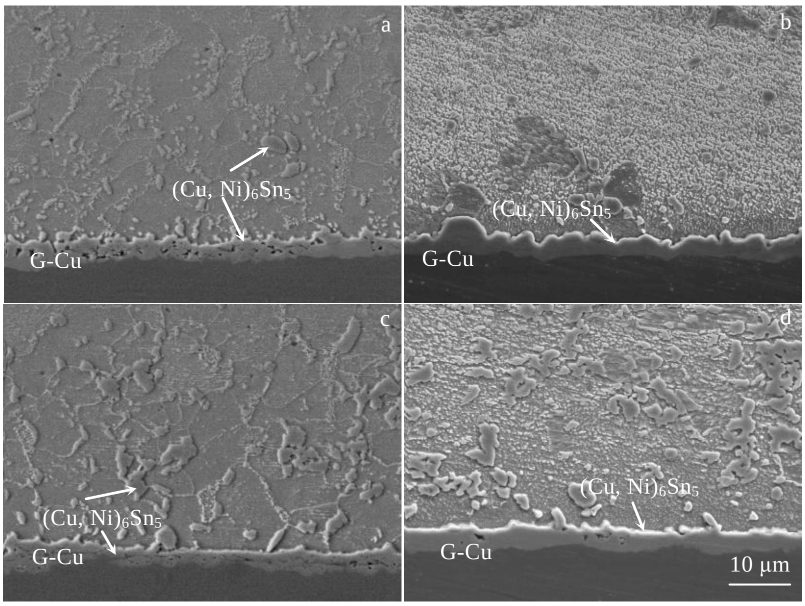

Fig.6 SEM images of the interfacial microstructure of SAC0705-*x*Ni/G-Cu interface after soldering and isothermal aging at 120 ℃ for 0 h (a, c) and 600 h (b, d): (a, b) SAC0705-0.05Ni, (c, d) SAC0705-0.3Ni

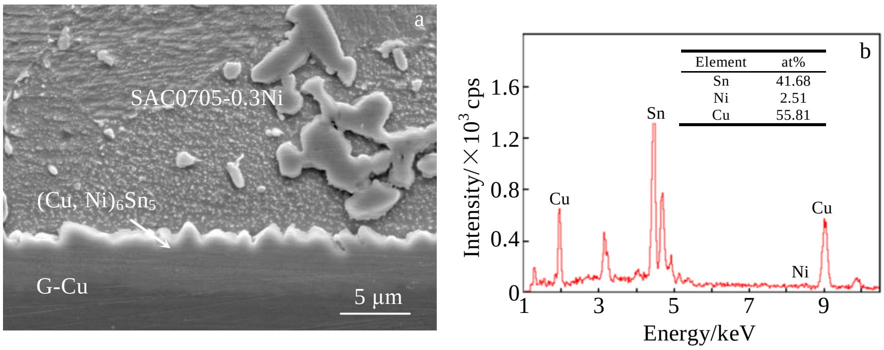

Fig.7 SEM image (a) and EDS spectrum (b) of SAC0705-0.3Ni/G-Cu interface aged at 120 ℃ for 600 h

for 0 and 600 h. Fig.6a and 6b correspond to SAC0705-0.05Ni/G-Cu system, and Fig.6c and 6d are SAC0705-0.3Ni/G-Cu system. It can be seen that only the (Cu, Ni)$_6$Sn$_5$ phase is clearly presented at the interface in Fig.6. Besides, when Ni is added in SAC0705, Cu$_6$Sn$_5$ becomes (Cu, Ni)$_6$Sn$_5$ in the solder bulk in Fig.6. Fig.7a shows microstructure of solder joint containing 0.3 wt% Ni, the (Cu, Ni)$_6$Sn$_5$ IMC layer near the solder consists of 41.68 at% Sn, 2.51 at% Ni and 55.81at% Cu, as shown in EDS result in Fig.7b.

It is illustrated that the growth of IMC grains is due to two kinds of kinetic processes[9]. One is ripening and the other is interfacial reactions. According to Fig.2a and 3a, it is found that Cu$_6$Sn$_5$ IMC layer is generated between the solder and the substrate in SAC0705/Cu and SAC0705/G-Cu solder joint. And as shown in Fig.4a, 4c, 6a and 6c, it is also seen that only (Cu, Ni)$_6$Sn$_5$ IMC layer appears in SAC0705-*x*Ni/Cu and SAC0705-*x*Ni/G-Cu solder joints. In the previous study[10,11], the corresponding reaction formulas are represented as follows:

$$6\text{Cu}+5\text{Sn}\rightarrow\text{Cu}_6\text{Sn}_5 \quad (2)$$

$$6(\text{Cu},\text{Ni})+5\text{Sn}\rightarrow(\text{Cu},\text{Ni})_6\text{Sn}_5 \quad (3)$$

Fig.8 demonstrates the relationship between the interfacial IMC thickness and aging time of SAC0705-*x*Ni/Cu solder joints, from which it can be obviously seen that the IMC thickness gradually increases as the aging time increases up to 600 h. The thickness of IMC in SAC0705/Cu solder joints is 2.06 μm after soldering, and it increases from 2.73 to 3.36 μm during isothermal aging. According to the data listed in Fig.8, the thickness of the interfacial IMC in the solder joints of SAC0705-*x*Ni/Cu increases first and then decreases. In addition, the thickness of the interfacial IMC in the solder joints of SAC0705-*x*Ni/Cu with little Ni element addition increases, and it decreases when the Ni content reaches 0.3 wt%. It is suggested that the IMC transforms from Cu$_6$Sn$_5$ into (Cu, Ni)$_6$Sn$_5$ with the addition of Ni elements. The increase of nucleation sites leads to the thickening of the IMC layer. However, Cu atoms are replaced by Ni atoms during the formation of (Cu, Ni)$_6$Sn$_5$. Then the diffusion of Cu atoms into the molten solder is

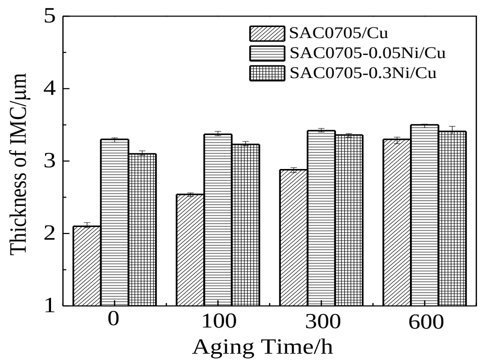

Fig.8 IMC thickness versus aging time in the solders with different Ni contents on Cu substrate

suppressed. Consequently, due to the increase of Ni content in the solder, the thickness of the (Cu, Ni)$_6$Sn$_5$ IMC layer shows a decrease trend.

Fig.9 shows the variation of the IMC layer thickness of SAC0705-*x*Ni/G-Cu solder joints. It is obviously seen that the thickness of interfacial IMC in SAC0705-*x*Ni/G-Cu becomes lower than that in SAC0705-*x*Ni/Cu system. The increase in Ni content has similar effects on the solder bulks on Cu and G-Cu substrates. The thickness of the interfacial IMC in the solder joints of SAC0705-*x*Ni/G-Cu increases first and then decreases. By comparing the IMC layers on the two kinds of substrates, it is found that the interfacial IMC on G-Cu substrate is relatively thin. This phenomenon approves that the grapheme-coated layer works as a diffusion barrier at the interface of the solder joints. Therefore, the formation and the growth of the interfacial IMC layers are suppressed.

Fig.10 clearly indicates the growth trend of the interfacial IMC as aging time increases from 100 to 600 h. It is obviously observed that the thickness of the IMCs increases almost linearly with the square root of aging time. Generally, the thickness of the IMCs layer formed under aging condition can be expressed by empirical power law equation:

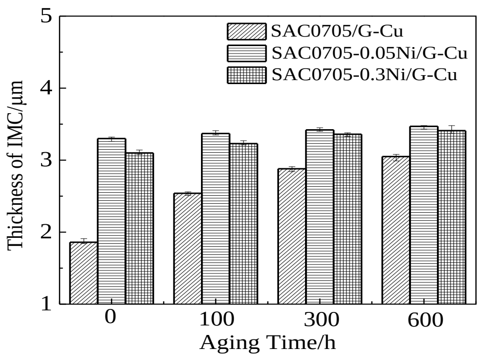

Fig.9 IMC thickness versus aging time in the solders with different Ni contents on G-Cu substrate

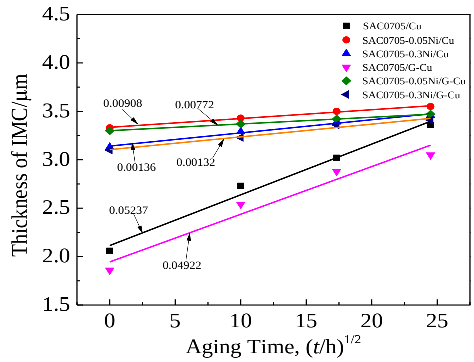

Fig.10 Relationship of thickness of IMC at soldering interfaces with square root of aging time

$$X = X_0 + At^n \quad (4)$$

where X is the thickness of the IMC layer at aging time t, X_0 is the initial thickness after only soldering, A is the IMC growth rate constant and t^n is the time exponent. Besides, Kim et al[12] studied that the growth of IMCs usually follows the linear or parabolic kinetics during the solid aging process. For parabolic kinetics, literature reported [13] that growth kinetics of IMCs is controlled by volume diffusion, i.e., n=0.5. Moreover, it is remarkably shown that the linear gradients for SAC0705/Cu, SAC0705-0.05Ni/Cu, SAC0705-0.3Ni/Cu, SAC0705/G-Cu, SAC0705-0.05Ni/G-Cu and SAC0705-0.3Ni/G-Cu are 0.052 37, 0.009 08, 0.0136, 0.049 22, 0.007 72 and 0.0132 μm/h$^{1/2}$ by fitting method from the experimental data, respectively. It means that interfacial IMC growth rate constant of SAC0705/Cu, SAC0705-0.05Ni/Cu, SAC0705-0.3Ni/Cu, SAC0705/G-Cu, SAC0705-0.05Ni/G-Cu and SAC0705-0.3Ni/G-Cu is 7.6×10^{-19}, 0.23×10^{-19}, 0.51×10^{-19}, 6.7×10^{-19}, 0.17×10^{-19} and 0.48×10^{-19} $m^2\ s^{-1}$, respectively. The IMC layer growth rate constant of SAC0705-xNi/Cu system (x=0, 0.05, 0.3, wt%) is higher than that of SAC0704-xNi/G-Cu. And when the Ni is added into solder, the growth rate constant of interfacial IMC layer is suppressed. According to the literature, Cheng et al[14] found that the Ni atom can accelerate the formation of Cu_6Sn_5 IMCs and replace some fractions of Cu in the Cu-Sn intermetallic compounds. Moreover, the thermodynamic bonding between Ni and Sn is stronger, compared with that between Cu and Sn. Thus, the phase stability for $(Cu, Ni)_6Sn_5$ is greater than that for Cu_6Sn_5[15]. The formed $(Cu, Ni)_6Sn_5$ layer is a good diffusion barrier that inhibits the interdiffusion among Sn, Cu and Ni atoms, which will limit the further growth of the IMC layer. By comparing the IMC layers on the two kinds of substrates, it is found that the interfacial IMC growth rate constant on G-Cu substrate is relatively low. The grapheme-coated layer on the Cu substrates does not participate in the reaction between Sn and Cu. It has similar function to the $(Cu, Ni)_6Sn_5$ layer, and also works as a diffusion barrier at the interface of the solder joints.

3 Conclusions

1) The scallop-like Cu_6Sn_5 layer forms between the SAC0705 solder and Cu or G-Cu substrates during soldering process. With increasing the aging time, the thickness of IMC layer increases continuously.

2) With the addition of Ni element, interfacial IMC transforms from Cu_6Sn_5 into $(Cu, Ni)_6Sn_5$. With the increase of Ni content, the thickness of the interfacial IMC in the solder joints of SAC0705-xNi/Cu and SAC0705-xNi/G-Cu increases first and then decreases. When the Ni content increases in SAC0705-xNi, the $(Cu, Ni)_6Sn_5$ IMC layer shows a smooth surface. And when the Ni is added into solder, the growth rate constant of interfacial IMC layer on two kinds of substrates is suppressed

3) The formation and the growth of the interfacial IMC are suppressed by the grapheme-coated layer. Compared with Cu substrate, the interfacial IMC growth rate constant on G-Cu substrate is lower.

References

1 Wierzbicka-Miernik A, Miernik K, Wojewoda-Budka J *et al*. *Intermetallics*[J], 2015, 59: 23
2 Liu L, Chen Z, Liu C *et al*. *Intermetallics*[J], 2016, 76: 10
3 Tao Q B, Benabou L, Vivet L *et al*. *Materials Science & Engineering A*[J], 2016, 669: 403
4 Li Yang, Ge Jinguo, Zhang Yaocheng *et al*. *Transactions of the Indian Institute of Metals*[J], 2017, 70(9): 2429
5 Zhang X, Hu X, Jiang X *et al*. *Applied Physics A*[J], 2018, 124(4): 315
6 Gao F, Takemoto T. *Journal of Alloys & Compounds*[J], 2006, 421(1): 283
7 Chen S, Brown L, Levendorf M *et al*. *Acs Nano*[J], 2011, 5(2): 1321
8 Lee T Y, Choi W J, Tu K N *et al*. *Journal of Materials Research*[J], 2002,17(2): 291
9 Kim H K, Tu K N. *Physical Review B: Condensed Matter*[J], 1996, 53(23): 16 027

10 Luo D X, Xue S B, Liu S. *Journal of Materials Science Materials in Electronics*[J], 2014, 25(12): 5195
11 Kim S H, Yu J. *Journal of Materials Research* [J], 2010, 25(9): 1854
12 Kim D G, Jung S B. *Journal of Alloys & Compounds*[J], 2005, 386(1): 151
13 Hu X, Xu S, Yang Y *et al*. *Materials Science & Engineering A*[J], 2014, 600(5): 67
14 Cheng F, Nishikawa H, Takemoto T. *Journal of Materials Science*[J], 2008, 43(10): 3643
15 Gao F, Takemoto T, Nishikawa H. *Materials Science & Engineering A*[J], 2006, 420(1-2): 39

Ni 添加量对铜基板和石墨烯铜基板的界面反应和 IMC 生长的影响

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摘 要：研究了钎焊与时效过程中，在 Sn0.7Ag0.5Cu（SAC0705）钎料与 Cu 基板和石墨烯 Cu 基板界面处金属间化合物(IMC)的形成与演变。采用加热平台制备焊接试样并在 120 ℃时效 600 h。结果表明，界面金属间化合物在时效过程中增厚。SAC0705/Cu 和 SAC0705/G-Cu 2 种焊接界面金属间化合物均为 Cu_6Sn_5。当钎料中添加 Ni 元素后，Cu_6Sn_5 化合物转变为 $(Cu, Ni)_6Sn_5$。随着钎料中 Ni 元素含量的增大，2 种基板上的界面金属间化合物厚度先增加后减小。此外，随着 Ni 含量增大，化合物生长速率降低。石墨烯 Cu 基板表面的石墨烯层起到扩散阻挡层效果，因此，石墨烯 Cu 板上的化合物厚度小于常规 Cu 基板，同时其界面化合物生长速率较低。

关键词：石墨烯铜基板；焊点；金属间化合物；镍元素

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