Investigations on Zn-Al-Ge Alloys as High Temperature Die Attach Material

A. Haque[1], Y. S. Won[2], A. S. M. A. Haseeb[1,*] and H. H. Masjuki[1]
[1] Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[2] ON Semiconductor, Package Innovation & Development Center (PIDC), SCG Industries Malaysia Sdn Bhd, Lot. 122, Senawang Industrial Estate, 70450 Seremban, Negeri Sembilan, W. Malaysia
[*]Corresponding author, Email: haseeb@um.edu.my, mobile: +60169817372

Abstract

Zn-Al based alloys have been suggested as high temperature lead-free solder for Si die attach by different researchers. But, so far, these alloys have not been tested in the industrial environment. In this study, Zn-Al-Ge alloy solder wire was used for Si die attachment on Cu substrate in an automatic die attach machine. The back side of the die was metalized with Ti/Ni/Ag layers. Die attachment was performed in a forming gas environment at temperatures ranging from 370°C to 390°C. Interfacial structure at the Si die and Cu substrate interfaces, and the bulk solder microstructure were investigated using an optical microscope, scanning electron microscope (SEM), energy dispersive x-ray (EDX) and electron probe microanalyzer (EPMA). Wetting characteristics and die shear strength were also studied.

Cross sectional microstructural investigation revealed that as many as three intermetallic (IMCs) layers form at the solder/copper interface. A CuZn intermetallic layer forms close to copper, a scallop shaped $CuZn_4$ forms at the solder side, while Cu_5Zn_8 forms at the middle. At the Si die-solder interface, with Ti/Ni/Ag metallization, no IMC layer was detected. Microstructural evidence suggests that Ni layer did not react with the Zn-Al-Ge solder. The microstructure of the bulk solder consists of mainly two phases: one with a lighter contrast and the other one being darker under the SEM. The phase with lighter contrast is a zinc rich phase containing an average of about 70.9% Zn. The darker one is found to be an aluminum rich phase containing an average of about 54.9% Al. In addition, some particles with brighter appearance are observed at different places in the bulk solder. These particles are rich in zinc and their composition closely resembles that of scallop type $CuZn_4$ IMC which forms at the solder side of the copper-solder interface. It is suggested that these particles are $CuZn_4$ IMC which have been spalled from the interface during soldering. Wetting of Zn-Al-Ge solder on Cu substrate was found to be lower at 370°C as compared with that at 390°C. Voids were found in the solder which were more in number at higher die attach temperatures. Die shear strength was found to be higher at the die attached temperature of 390°C (22.3 MPa) as compared with those obtained at 370-380°C (15.5-17.4 MPa). Die shear strength of standard Pb-Sn solder was also measured for comparison and was found to be 28.2 MPa. The microstructure and properties of the solder joint are discussed.

Key words: Zn-Al alloy, high temperature solder, die attach, Cu substrate, interfacial reaction, lead-free

Introduction

Lead is an ideal material for soldering electrical contacts because it melts easily, has excellent wettability, high ductility, low Young's modulus, maintains a reliable connection, and is relatively inexpensive. On the other hand, high-lead solder has high melting temperature (>260°C) which is suitable for the reflow process. But RoHS directive (2002/95/EC) restricts the use of six hazardous materials such as lead, mercury, cadmium, hexavalent chromium (Cr6+), polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE) in the manufacture of electronic and electrical equipment [1]. However, appropriate substitute of high-temperature Pb-free solder have not been established yet [2-6]. As a consequence, Pb-based solders are still used in the consumer electronic products together with Pb-free solders that hamper the recycling process [7, 8]. Currently semiconductor industries are looking for high temperature lead-free solders for attaching the semiconductor chips to the substrates (lead-frame). This is due to the regulatory requirement and increasing consumer pressure to remove lead from the semiconductor assembly. As a result, lead-free solder has become an important production factor for the semiconductor industry [9]. For some technical and commercial reasons the lead-free products are prevented from entering into the market. Currently about 150 tons/year of high Pb-solders are used for die attach applications of which most of it as solder wire, ribbon or preform [9]. The solder die attach is predominantly done in sophisticated, fully automated production lines. Therefore, the properties of the lead-free solder materials should be within acceptable limits of the present production conditions such that it avoids major capital expenses. For that reason, the industry is looking for drop-in replacement of the Pb-based solder which will minimize the financial impacts as well as better opportunity to successfully market the product.

The solder alloys used in die attach usually are in the range of 275-345°C (liquidus), either to resist subsequent reflow during surface mounting, or, in the case of power devices, to allow higher device operating temperatures without joint failure. A suitable substitute for high-lead solder alloys requires: material processing at temperatures below 400°C; no re-melt until a temperature of at least 260°C is reached; good adhesion on conventional part surfaces; good resistance against thermal fatigue; good wetting on leadframe, low void rate on the die-attach layer and of course, no lead in the composition. Typically, for power and high-power applications, maximum void rate allowed is 5% [10].

Limited number of alloying systems are available for high-temperature lead-free solders. These are Sn-Sb, gold alloys, bismuth based alloys, Sn-Cu alloy or composites, and zinc based alloys [8]. Among these, Zn-Al has a long history of use as a high-temperature solder for aluminum alloys mainly for structural purposes [11, 12]. The Zn-Al binary alloy has an eutectic temperature of 380^{o}C at 6 wt.% aluminum and this alloy does not form any intermetallic compounds. By adding a third element such as copper, magnesium, or germanium, the melting temperature can be decreased to below 350^{o}C [13-16].

Although, Zn-Al base alloys have been suggested as candidates for the Pb-free high-temperature solder by different researchers [17], these alloys have not been tested in an industrial setting. In this study, Zn-Al-Ge alloy solder wire was used for Si die attachment on Cu substrate in an automatic die attach machine. Interfacial structure at the Si die and Cu substrate interfaces, and the bulk solder microstructure were investigated.

Experimental Procedure

Zn-Al-Ge solder wire of diameter 0.5 mm was used for Si die attachment on Cu substrate using automatic die attach machine. The size of the Si dies was approximately 1.9 mm x 1.2 mm x 0.3 mm. The back side of the die was metalized with Ti/Ni/Ag layers. The thickness of the Cu substrate was approximately 0.5 mm. Die attachment was performed in a forming gas environment at temperatures ranging from 370^{o}C to 390^{o}C. Cu substrate was preheated by the machine before dispensing solder on it. Each of the die was attached within a short period of time of approximately 0.8 second. After die attachment, the Cu substrate with Si dies was cooled down to room temperature by natural convection cooling.

Interfacial structure at the Si die and Cu substrate interfaces, and the bulk solder microstructure were observed using optical microscope (OM) and scanning electron microscope (SEM: Hitachi S-3400N) and analyzed by energy dispersive x-ray (EDX), and electron probe microanalyzer (EPMA: CAMECA SX100). The thickness of each IMC layers formed at the Cu substrate interface during soldering was determined based on the average data for each soldering conditions. Shear strength of the Si die attach joints were measured using a die shear machine (STORM INTELLI TEST FA1500) with a stroke length of 3000 µm and a test height of 100 µm from the bottom of the specimen. Void areas in the solder joints were determined by through scan X-ray machine (Sonix scan, Model: UHR 2000). Wetting on Cu substrate was evaluated by measuring the diameter of the soldered area. For measuring the soldered area, reference X and Y axis were set first. Then five points were picked at the periphery of the soldered area. Based on the reference axis and five points, wetting circle diameter was calculated using Smart scope software.

The melting behavior of the solder wire was determined from heating curve obtained by differential scanning calorimetric (DSC) measurement at a heating rate of 10^{o}C/min.

Results and Discussion

DSC heating curves for the Zn-Al-Ge solder wire is presented in Fig. 1. The first endothermic peak appeared at 282^{o}C due to the monotectoid reaction of Al-rich face centered cubic (fcc) and hexagonal close-packed (hcp) (Zn) which converted to Zn-rich fcc, as shown in the Zn-Al phase diagram in Fig. 2 [17]. The second large endothermic peak appeared at 357^{o}C where eutectic melting reaction was occurred and Zn-rich fcc & hcp (Zn) becomes liquid in this stage. Though the eutectic melting temperature of Zn-Al binary system is 380^{o}C, it is found lower due to the addition of Ge in this alloy.

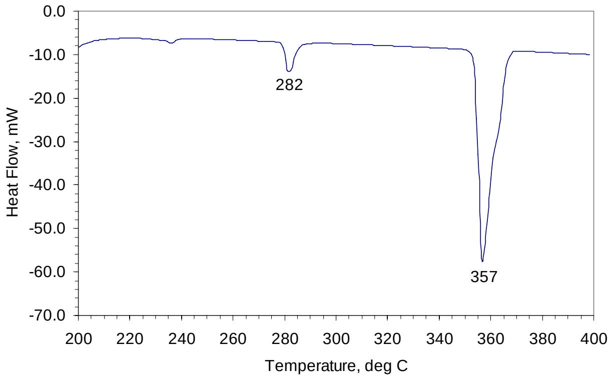

Fig. 1: DSC results of Zn-Al-Ge solder wire

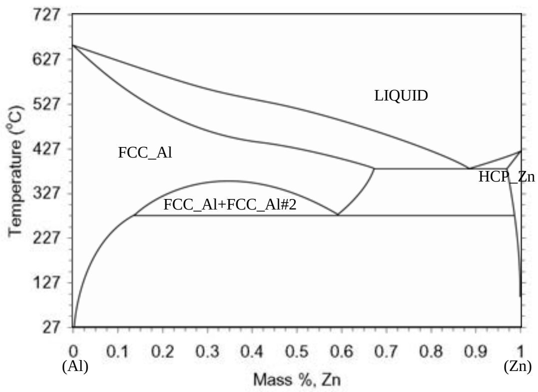

Fig. 2: Phase diagram of Zn-Al binary system [18]

Fig. 3 shows SEM images of typical bulk and interfacial microstructure of a Si die-solder-copper system. The IMC layers are observed at the Cu substrate-solder interface. At the Si die-solder interface (Fig. 3a); with Ti/Ni/Ag metallization at the die back, no IMC layer was detected. Microstructural evidence suggests that Ni layer did not react with the Zn-Al-Ge solder.

The microstructure of the bulk solder (Fig. 3a) consists of mainly two phases: one with a lighter contrast and the other one being darker. EDX analysis was carried out on these points. The phase with lighter contrast (point A) is a zinc rich phase containing about 70.9 wt.% Zn. The darker one (point B) is found to be an aluminum rich phase containing about 54.9 wt.% Al. In addition, some particles with brighter appearance (point C) are observed at different places in the bulk solder. Details of these particles are discussed later.

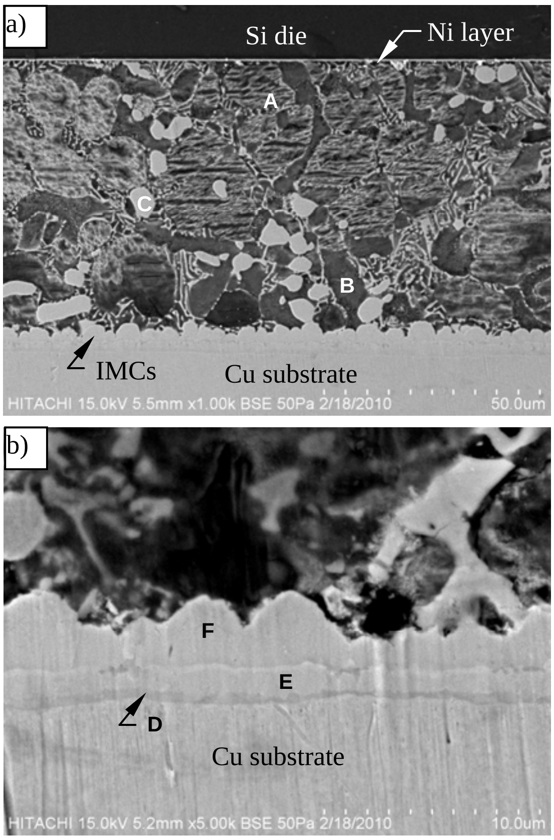

Fig. 3: SEM images of the die attached sample at 390°C represents: a) bulk microstructures; b) IMC layers

EDX analysis results of the bulk solder are presented in Table 1.

Table 1: EDX analysis results of bulk microstructure

Element	Point A		Point B		Point C	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Al K	5.1	11.3	54.9	74.5		
Cu L	22.2	21.5	14.1	8.3	20.0	20.5
Zn L	70.9	65.8	24.5	13.9	80.0	79.5
Ge L	1.8	1.4	6.5	3.3		

From Fig. 3b it is evident that there are three distinct IMC layers that formed at the Cu substrate-solder interface. A thin layer (D) of β´-CuZn forms close to copper substrate, a scallop shaped ε-$CuZn_4$ layer (F) forms at the solder side and while γ-Cu_5Zn_8 layer (E) forms at the middle. The average thickness of each IMC layer was measured for different die attached temperature. Higher die attached temperature corresponds to greater IMCs thickness. The thin β´-CuZn layer varies from about 0.5 to 0.84 µm, γ-Cu_5Zn_8 layer from about 1.1 to 1.7 µm and ε-$CuZn_4$ layer from about 2.2 to 3.4 µm depending on die attached temperature. EDX was used to determine the chemical composition of these IMC layers. The measured composition of these IMC layers are given in Table 2.

Table 2: EDX analysis results of IMC layers

Element	β´-CuZn (D)		γ-Cu_5Zn_8 (E)		ε-$CuZn_4$ (F)	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Cu L	51.3	51.9	37.6	38.2	27.6	23.4
Zn L	48.7	48.1	62.4	61.8	72.4	76.6

The brighter particles that observed at different places in the bulk solder are rich in zinc and their composition closely resembles that of scallop type $CuZn_4$ IMC which forms at the solder side of the copper-solder interface. The shape and size of these particles are similar to that of $CuZn_4$ scallop. It is therefore suggested that these particles are $CuZn_4$ IMC which have been spalled from the interface during soldering.

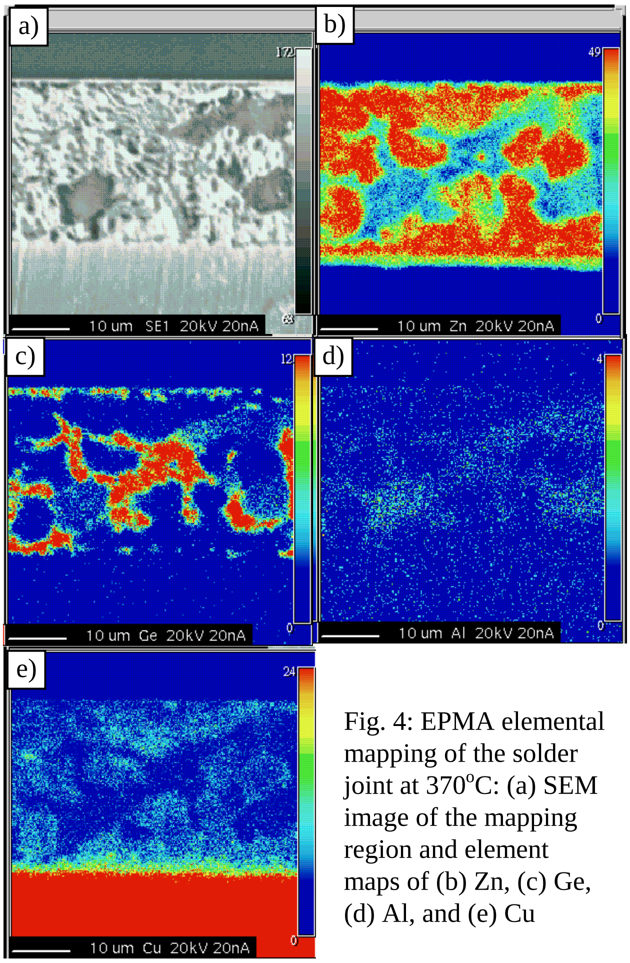

Fig. 4: EPMA elemental mapping of the solder joint at 370°C: (a) SEM image of the mapping region and element maps of (b) Zn, (c) Ge, (d) Al, and (e) Cu

Fig. 4 represents the EPMA elemental mapping of the solder joint prepared at 370°C. It is seen from the mapping that Zn and Cu existed at the same locations. It is to be mentioned that during soldering process, the Cu substrate is consumed by Zn (Fig. 5). The formation and growth of the IMCs take place simultaneously at the soldered interface as indicated in the Zn-Cu binary phase diagram (Fig. 6) [17]. On the other hand, Ge existed with

Al. From the binary phase diagrams of Al-Ge and Zn-Ge it is seen that there are eutectic points where Ge content is about 28 wt.% and 5 wt.% respectively[19]. Since Ge has eutectic point at higher concentration in the Al-Ge binary system than in the Zn-Ge binary system, it is expected that Ge existed with Al in the Zn-Al-Ge solder.

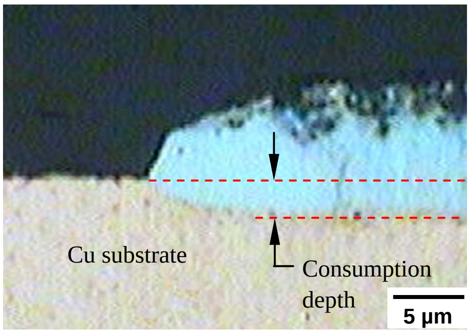

Fig. 5: Consumption of Cu substrate during soldering

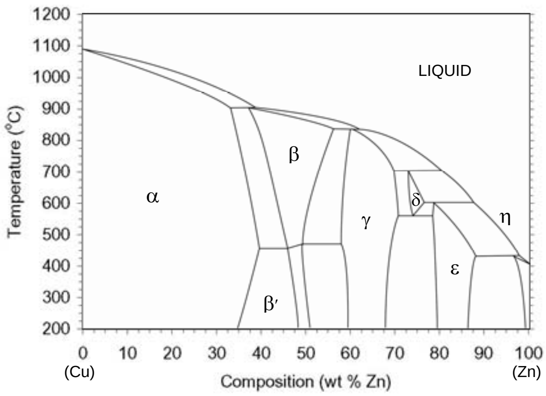

Fig. 6: Phase diagram of Zn-Cu binary system[20].

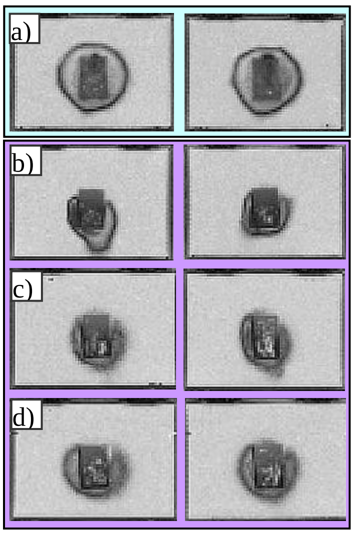

Fig. 7: Through scan x-ray image of die attach samples: a) Standard Pb-Sn solder wire was used, and Zn-Al-Ge solder wire was used at b) 370^{o}C, c) 380^{o}C, & d) 390^{o}C

Fig. 7 shows the X-ray images of the die attached samples. The darker rectangular area is Si die and the outer circular area is wetting area of the solder. Die attached samples were scanned with through scan x-ray for analyzing the void conditions. These results were compared with that of the standard Pd-Sn solder joints. From the x-ray analysis it is found that die attached samples at 390^{o}C has more voids, represented by light spots in the die, as compared with at 370^{o}C. It is to be mentioned here that void area of all the die attached samples are found more than 5%. Development of such voids during soldering depends on the soldering temperature due to Kirkendall effect resulting from the difference of diffusivity between Cu and Zn which may increase during its high temperature application [17].

It is also observed that wetting of Zn-Al-Ge solder on Cu substrate is lower at 370^{o}C compared with that at 390^{o}C (Fig. 8).

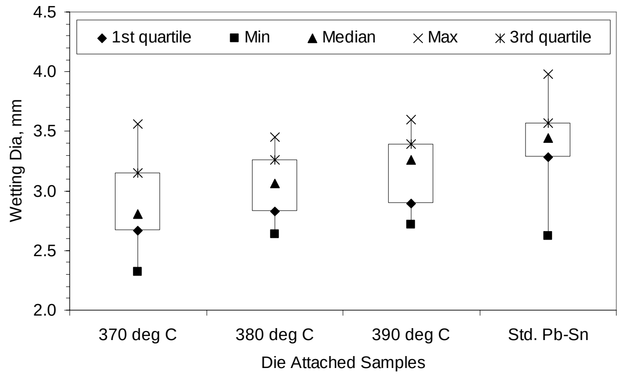

Fig. 8: Wetting diameter of the solder joint on Cu substrate at different die attached temperature

Die shear strength was also measured for Zn-Al-Ge solder joints and compared with the strength of standard Pb-Sn solder joints (Fig. 9). It is found that shear strength is higher at the die attached temperature of 390^{o}C (22.3 MPa) as compared with those obtained for 370-380^{o}C (15.5-17.4 MPa). Die shear strength of standard Pb-Sn solder is found 28.2 MPa which is higher than

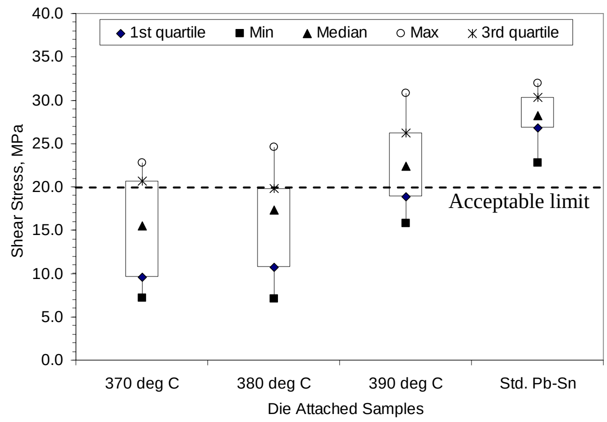

Fig. 9: Die shear strength at different die attached temperature

the strength of Zn-Al-Ge solder. In industry, the acceptable limit for the die shear strength is considered as 20 MPa for both solder and epoxy die attach.

Conclusions

Interfacial structure at the Si die and Cu substrate interfaces, and bulk microstructure of Zn-Al-Ge solder was investigated in samples prepared in an industrial setting. The formation of three IMC layers such as β´-CuZn, γ-Cu_5Zn_8 and ε-$CuZn_4$ were observed at the solder-Cu substrate interface. Some particles with brighter appearance which chemical composition closed to $CuZn_4$ were observed at different places in the bulk solder. Wetting on Cu substrate was found better at higher die attached temperature which is closed to the maximum operating temperature of the Si die. On the other hand, more voids were found at higher die attached temperature. Die shear strength of Zn-Al-Ge solder joint varies from 15.5 to 22.3 MPa depending on the die attached temperature which was lower than that of standard Pb-Sn solder (28.2 MPa). But shear strength at higher die attached temperature is within the acceptable limit (20 MPa).

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