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Diffusion soldering using a Gallium metallic paste as solder alloy: study of the phase formation systematics

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Abstract In this work preliminary results are reported on the characterization of Pb-free joints produced by using a diffusion soldering method at a process temperature of 700 °C during 20 min. The solder alloy is a metallic paste involving Ga and Al and Ni powder, and the substrates are Cu and Ni. The dissolution and diffusion-reaction processes, which take place at the interfaces of the interconnection zone, have been investigated by means of SEM and EPMA. A solid solution and intermetallic compounds (IMCs) with high melting point form as layers almost free from defect, allowing service temperatures about 500 °C higher than the process temperature. The phase stability sequence starting from the Ni to the Cu interface is the following: α'-Ni_3Ga, γ-Cu_9Ga_4, β-Cu_3Ga and (Cu) solid solution of the Ga–Cu system. The relative reaction front displacement of the layers and the implications of the present findings for the applicability of the diffusion-soldering method are also discussed.

Introduction

The study of new Pb-free solders has become an important research field, particularly because of the new environmental restrictions and the increasing requirements for the bond reliability in the electronic and microelectronic industry. The recent directives of the European Union (RoHS—Restriction of the use of certain hazardous substances in electrical and electronic equipment, WEEE—Waste Electrical and Electronic Equipment) urge to produce devices avoiding completely the usage of lead by the middle of 2006 [1, 2]. Furthermore, these restrictions concern the maximal concentration allowed for other hazardous substances like Pb, Hg, Cd, and Cr (VI) as 0.1 wt.% with the aim to protect the health of the people and the environment in general. Therefore, important research efforts have been devoted for the development of Pb-free alloys [3–6]. In particular, the thermodynamic assessment of several alloys of interest for practical applications has received a large impulse from the use of the so-called CALPHAD techniques [7–9].

In addition to the environmental restrictions, the Pb-free solder candidate alloys for applications have to satisfy a long requirement list: good wetting ability of the substrates; ability to form a strong bond with the substrates; convenient melting and solidification point for the joint process; good mechanical behavior in terms of toughness and resistance to mechanical and thermal fatigue; good corrosion resistance; high thermal and electrical conductivity. Furthermore, the alloy should allow a simple assembly for the components, and offer low material and process costs [10, 11].

The diffusion soldering seems to be an attractive method due to the advantages of relatively short times and low process temperatures in comparison with the high service temperatures and the good mechanical behavior offered by the bond. This joint technique belongs to the family of the Transient Liquid Phase Bonding (TLP)

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methods. It consists in melting a thin layer of an alloy between the substrates inducing diffusion-reaction during the isothermal solidification of intermetallic compounds (IMCs) in order to join the substrates [12–15]. This methodology finds a wide application field, from microelectronics to airspace industry [16–18]. The success of the method depends strongly on a careful solder selection according to the substrates, with the avoidance of the formation of phases which can deteriorate the reliability of the joint.

The purpose of the present paper is to present the results of a preliminary characterization of diffusion-soldered bonds produced by adopting a metallic paste consisting of Ga and Ni, Al, and Cu as the joint material in order to join a Ni to a Cu substrate. These materials were chosen because of their wide use in the electronic and coating industries. Gallium was selected because this element presents some interesting properties, viz., a very low melting point, 29.78 °C [19], a volumetric expansion during solidification of 3.4% [19, 20], a good wetting ability with almost all the materials used in electronics [21], and the possibility of forming with Al, Cu, Ni solid solutions and IMCs with high thermal stability [22, 23]. Moreover, the addition of Ga to an alloy increases the wetting ability, the ductility and the tensile strength, while decreasing the liquidus temperature [24].

Experimental procedures

The Ni and Cu substrates (99.999%) were sectioned and polished with diamond paste in order to obtain discs with 10 mm diameter, 0.25 mm thickness and a mirror-like finishing surface. The metallic paste was prepared with Ga (99.99%) and powder of Al and Ni (99.99%) with an average grain size of 10 μm. Two paste compositions in weight percent were selected, viz., 15Al–40Ni–45Ga and 45Al–55Ga, respectively.

A thin layer of metallic paste was located between the Cu and Ni substrate under a light compression in order to guarantee a parallel interconnection zone. The assembly was encapsulated and heat-treated under a vacuum level of 10^{-4} mbar at 700 ± 3 °C during 20 min. After the annealing, the capsules were quenched in water.

The samples were prepared for the analyses using the proper metallographic procedure of polishing with paper and diamond paste until 0.25 μm. The cross sections of the interconnection zones were examined by means of optical and electron (SEM) microscopy. Compositions versus distance relations were determined by using electron probe microanalyzer (EPMA).

Results and discussion

Diffusion and phase stability systematics

The optical micrographs of Cu/Al–Ga–Ni/Ni bonds produced by annealing at 700 °C during 20 min are shown in Fig. 1. Three different layers indicated as A–C may be distinguished between the Cu and Ni substrates in the 50 μm interconnection zone of Fig. 1, which appear almost free from pores or cracks. In Fig. 2 the morphology developed on the Cu and Ni free surfaces through the interaction with metallic paste may be observed. The layer on the Cu side is found to be thicker than the ones on the Ni side. In addition, the reaction front on the Cu side has migrated preferentially into the Cu substrate, while the reaction front on the Ni side moved preferentially into the metallic paste. These observations suggest, in the first place, that a diffusion process has occurred with the elements of the paste moving through the new formed C layer, reaching the Cu solid interface and reacting at that point. Second, Fig. 2 also suggests that the Ni atoms of the Ni substrate diffuse preferentially through the new-formed phases reaching the liquid/paste interface, and reacting there.

The morphology of two homogeneous layers formed on the Cu surface are shown in detail in Fig. 3. The closest layer to Cu forms through the interaction with the metallic paste and the other layer corresponds mainly to the reaction between the elements of the remaining paste, where the original Al and Ni grains are not observed. The latter is probably due to a liquid sintering process occurring in the paste at 700 °C, i.e., a temperature lower than the melting points of the Ni grains. Taking into account that the mobilities and the diffusion coefficients generally increase with the decrease of the melting points of the element [25–28], it is natural to presume that the larger thickness of the

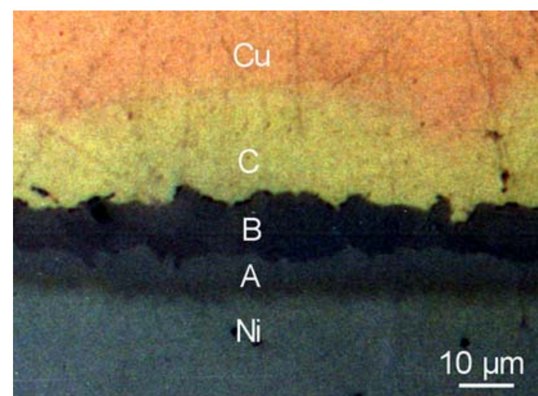

Fig. 1 Optical micrograph of the cross section of a Cu/Al–Ga–Ni-paste/Ni bond produced by annealing at 700 °C during 20 min

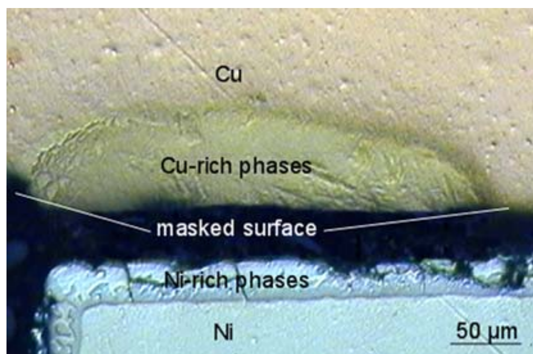

Fig. 2 Optical micrograph of cross sections of the Cu/Al–Ga–Ni-paste and Ni/Al–Ga–Ni-paste interfaces produced by annealing at 700 °C during 20 min, where the original paste was completely consumed

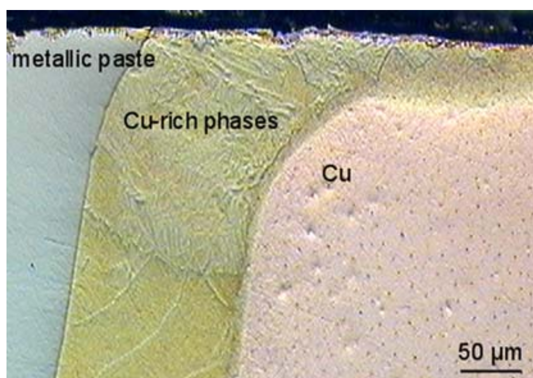

Fig. 3 Optical micrograph of the cross section of the Cu/Al–Ga–Ni-paste interface produced by annealing at 700 °C during 20 min

C region (Fig. 1) is related with the larger expected mobility of the Ga atoms.

In Fig. 4, three layers grown on the Ni surface are observed, one of which shows a globular morphology growing preferentially towards the liquid paste. This suggests that the Ni atoms of the Ni substrate migrate through the formed layer reaching the liquid interface and reacting with the paste.

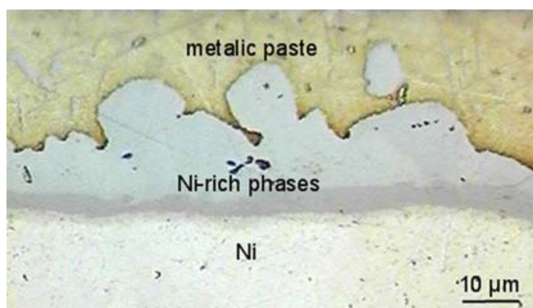

Fig. 4 Optical micrograph of the cross section of the Ni/Al–Ga–Ni-paste interface produced by annealing at 700 °C during 20 min

Phase composition and stability considerations

In order to identify the layers formed, EPMA analyses were performed to determine the composition versus distance relations with a spatial resolution of approximately 1 µm diameter. These results are presented in Figs. 5a and 6a for the Cu/Al–Ga–Ni/Ni and Cu/Al–Ga/Ni bonds, respectively, produced by annealing at 700 °C during 20 min. In the first place, Ni-rich (A) and Cu-rich regions (B–D) can be distinguished, whereas the Al content is almost negligible. The dark circles on the micrographs of Figs. 5b and 6b indicate the scanning path transverse to the layers. The average composition values obtained by means of EPMA for these various layers are summarized in Table 1.

Although diffusion soldering cannot be considered as an equilibrium process, the attainment of a local equilibrium at the interfaces might be assumed as a reasonable approximation [25–28]. Therefore, direct reference to the equilibrium phase diagrams will be made, even if some equilibrium IMCs might be absent due to kinetic reasons or metastable phases might appear in the interconnection zone [25–28]. More specifically, in the present work the most probable IMCs will be selected on the basis of average composition values (Table 1) and the phase-equilibrium relations corresponding to the process temperature 700 °C. By considering the concentration of the Cu, Ni, and Ga elements, various binary interactions might in principle be

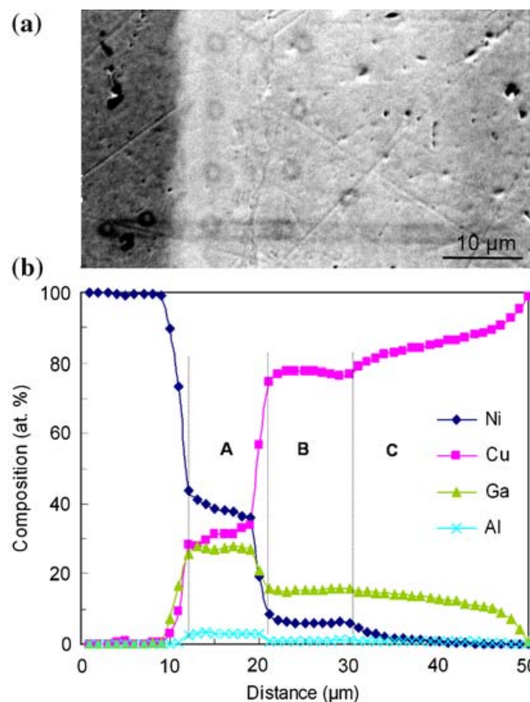

Fig. 5 Composition versus distance relations (**a**) established by EPMA across the interconnection zone and micrograph (**b**) of the Cu/Al–Ga–Ni/Ni bond produced at 700 °C and 20 min

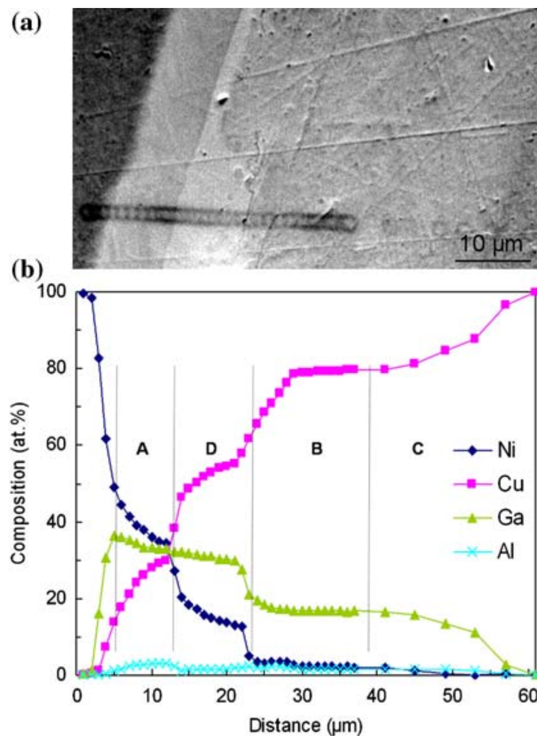

Fig. 6 Composition versus distance relations (**a**) established by EPMA across the interconnection zone and micrograph (**b**) of the Cu/Al–Ga/Ni bond produced at 700 °C and 20 min

considered as the relevant ones, namely, Cu–Ni, Cu–Ga, Ga–Ni, and the ternary interaction Cu–Ga–Ni. Since, the ternary phase diagram is in fact not available, the discussion will be based on adopting as a useful guide, the binary equilibrium diagrams [22, 23]. The Cu–Ni phase diagram presents total solubility, while the Cu–Ga and Ga–Ni show a number of IMCs and wide solid solution regions with high thermal stability.

The Ni concentration in the A region of the cross sections of Figs. 5a and 6a is slightly larger than that of Cu, but not larger enough to be considered as dominant. However, by considering that the A region (Fig. 1) seems to correspond to the IMCs developed onto the Ni surfaces (Fig. 4), it will be tentatively assumed that the relevant binary system here is the Ga–Ni. Hence, by considering the average composition of Ga and the Ga–Ni phase diagram at 700 °C, it might be suggested that the A region probably corresponds to a α'-Ni_3Ga phase, stable in the Ga–Ni phase diagram, which has incorporated atoms of Cu in the crystal structure. More precisely, the data in Table 1 suggest for this phase a simplified formula of the type $(Ni,Cu)_{0.75}Ga_{0.25}$.

Since, the concentration of Cu in the B–D regions (Figs. 5a, 6a) is clearly the largest, the Cu–Ga system will be considered as the relevant one. The composition versus distance data for Cu shows steps in the B and the D regions, while the C region is characterized by a weak concentration gradient, which might very well correspond to the (Cu,Ga) solid solution of the Cu–Ga system. Indeed, the maximum experimental content of Ga in the C region, is compatible with the wide stability range of the (Cu,Ga) solid solution at 700 °C, which extends from 0 to almost 20 at.% Ga in the equilibrium diagram [22, 23].

According to the Cu–Ga phase diagram, the IMC in equilibrium with the (Cu,Ga) solid solution is the β-Cu_3Ga phase, which could be related to the B region adjacent to the C region in Figs. 5 and 6. It should be noted, however, that at 700 °C the β-Cu_3Ga phase is stable for Ga contents between 23 and 27 at.%, while the presently measured composition values of B region range from 15 to 17 at.% Ga. More precisely, the data in Table 1 suggest for this phase a simplified formula of the type $(Cu,Ni)_{0.83}Ga_{0.17}$ and $(Cu,Ni)_{0.85}Ga_{0.15}$ for the both kind of samples. One explanation for this discrepancy between the equilibrium and the experimental data might be the instability generated by the Ni atoms in the crystal structure of the (Cu,Ga) solid solution, forcing to re-order the structure into the next

Table 1 Average composition values obtained across the interconnection zone using EPMA in bonds produced at 700 °C and 20 min

Regions	Composition (at.%)				Simplified formula	Equilibrium phase
	Al	Cu	Ga	Ni		
Cu/Al–Ga–Ni/Ni						
A	3.07	28.75	26.65	41.53	$(Ni,Cu)_{0.75}Ga_{0.25}$	α'-Ni_3Ga
B	0.96	78.55	15.27	5.22	$(Cu, Ni)_{0.85}Ga_{0.15}$	β-Cu_3Ga
C	0.82	85.30	12.32	1.56	(Cu,Ga)	(Cu)
Cu/Al–Ga/Ni						
A	2.62	25.11	34.00	38.27	$(Ni,Cu)_{0.75}Ga_{0.25}$	α'-Ni_3Ga
B	1.76	78.57	16.85	2.42	$(Cu, Ni)_{0.83}Ga_{0.17}$	β-Cu_3Ga
C	0.65	85.50	12.81	1.04	(Cu,Ga)	(Cu)
D	1.53	52.32	30.62	15.53	$(Cu,Ni)_{0.69}Ga_{0.31}$	γ-Cu_9Ga_4

equilibrium phase. Other explanation is of course that the B region corresponds to a Cu–Ga–Ni ternary phase with a narrow composition range.

Analogously, the data in Table 1 suggest that the D region (Fig. 6a) probably correspond to the γ-Cu_9Ga_4 phase, which coexist with the β-Cu_3Ga phase in the equilibrium diagram. Specifically, the data of Table 1 suggest for the γ phase a formula of the type $(Cu,Ni)_{0.69}Ga_{0.31}$. Alternatively, the D region might correspond to a Cu–Ga–Ni ternary phase. Finally, the occurrence of the additional D layer in the Cu/Al–Ga/Ni bonds, which corresponds to the Cu-rich phase γ-Cu_9Ga_4, is due to the absence of Ni in the metallic paste.

Implications for technological applications

According to the present interpretation of the results, the IMCs formed in the interconnection zone might be attractive for their high thermal stability. The maximum temperatures at which the binary IMCs are stable in the binary phase diagrams open up the possibility of a high tolerance of the bonds to high-service temperatures, viz., α'-Ni_3Ga (1,220 °C), β-Cu_3Ga (915 °C), γ-Cu_9Ga_4 (836 °C). In particular, considering the Ni/Ni bonds where the α'-Ni_3Ga phase forms, the difference between service and process temperature might be larger than 500 °C. The difference might be enlarged for all the bond combinations Cu/Cu, Ni/Ni and Cu/Ni, by decreasing the process temperature since the mentioned IMCs are stable at room temperature. Obviously, decreasing the process temperature will cause an increase in the process time depending on the interconnection thickness. Therefore the actual service temperature should be determined on the basis of thermal stability tests, including thermal cycling.

The processing time is an important variable in industrial applications which depends crucially upon the interconnection thickness. The thickness can be reduced until a critical value is reached which depends upon the mechanical behaviour required for the bonds, in turn depending strongly on the morphology of the IMCs formed, grain size and orientation, among others factors. The thickness of the interconnection zone can be reduced by different methods, i.a. by using finer powders in the paste, by applying higher mechanical pressure during process, or by depositing the joint materials as thin layers using sputtering and laser ablasion for Ga deposition [11].

The fairly plane topography of the cross section of the Fig. 3 indicates similar hardness for the two layers. Such a characteristic is quite convenient to ensure a good mechanical behavior of the bond. The topography shown in Fig. 4 reveals on the other hand two levels, the deeper plane corresponding to the metallic paste after solidification and the uppermost plane corresponding to the growing IMCs layers and the Ni substrate, which are harder than the remaining paste. It can be also observed that the layers are almost free from defects. In addition, the interfaces close to the Cu and Ni substrates present a gradual variation (Figs. 1–4) instead of sharp changes. This may be taken as an indication of a good adhesivity of the parts and reasonably strong bonding of the substrates.

Indeed in order to corroborate the good quality or the reliability of the bonds several tests should be performed, i.a., thermal, electrical, corrosion, and mechanical tests. Furthermore, through a detailed study of the growth-rate of the layers, especially in experiments with static markers, it might be possible to determine the diffusion coefficients and to establish whether the diffusion-reaction process is diffusion or reaction controlled [25–28]. Besides, a complete phase identification requires a study of the crystal structure of the layers [25–28] by means of electron diffraction analyses by using XRD and TEM. These various studies are in progress in our laboratory, and the results will be reported elsewhere.

Conclusions

The interconnection zone of the Cu/Al–Ga/Ni and Cu/Al–Ga–Ni/Ni bonds developed at 700 °C and 20 min are almost free from defects, in particular at the substrate interface. Additionally, the layers formed seem to have similar hardness. These findings suggest that the diffusion soldering method can be effective to join two dissimilar substrates like Cu and Ni.

The preliminary results obtained using EPMA allow a tentative identification of the phases in the multilayer interconnection zone and points to the formation of various IMCs with high thermal stability. The interconnection zones of the Cu/Al–Ga/Ni bonds show four layers which have been tentatively described using the following simplified formulae: (Cu,Ga) solid solution, $(Cu,Ni)_{0.85}Ga_{0.15}$, $(Cu,Ni)_{0.69}Ga_{0.31}$, $(Ni,Cu)_{0.75}Ga_{0.25}$. Three of these phases are directly related to the binary IMCs appearing in the equilibrium diagrams β-Cu_3Ga, γ-Cu_9Ga_4, and α'-Ni_3Ga, respectively. Similarly, the Cu/Al–Ga–Ni/Ni bonds show only three layers in the interconnection zones, viz., the (Cu,Ga) solid solution and the IMCs related to the binary β-Cu_3Ga and α'-Ni_3Ga structures.

The migration of the reaction front of the C layer, attributed to the (Cu,Ga) solid solution, indicates a preferential mobility of the Ga atoms through this forming layer towards the interface C region/Cu, where the reaction takes place. The atoms of the Ni substrate show a preferential mobility in the direction of the melted metallic paste, in order to reach the A region/liquid interface where a solid/liquid reaction takes place. The diffusion process

occurs through the growing A region, which has been classified in the present work as a α'-Ni_3Ga structure.

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