Lead-Free Fluxless Soldering below 120 °C

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ABSTRACT
This recent study demonstrates that Gallium-Copper alloys can be used for Pb-free fluxless soldering below 120 ºC. A number of GaCu-alloy pastes with Ga to Cu ratio 1 to 2 were formulated in the solid state using spherical (particle size > 20 μm - < 70 μm) Cu- and Ga-powders. The latter powder was fabricated using a specially developed cryo-pulverization technique followed by sieving to the fraction < 32 μm. Several soldering pastes were also prepared by mechanical blending of the Cu-powder into liquid Ga.

It was found that when alloy paste made of Cu- and Ga-powders in the ratio 2 to 1 is used for soldering at 120 ºC to Cu-substrates, the Ga-based liquid present in the soldering paste is completely converted into $CuGa_2$ intermetallic after 16 hours and the product joint contains many voids. When, on the other hand, the solder paste was formulated by mechanical blending of the Cu-powder into liquid Ga, voiding inside the interconnect structure was found to be insignificant.

The newly developed GaCu-alloy pastes can also be used for soldering below 120 ºC to Ag-substrates. However, very fast kinetics observed in the reaction of Silver with liquid Gallium results in a heavy wicking of the liquid (Gallium) constituent from the GaCu-alloy paste leading to significant voiding in the interconnect structure.

It was also shown that because of the very fast reaction kinetics in the Ag / liquid system, the use of Ga-based interlayer allows Transient Liquid Phase (TLP) bonding of Ag-substrates to be readily accomplished at temperature below 120 ºC, and the product interconnection can be operated at significantly higher temperature.

Reactive phase formation at the contact surfaces within the soldered interconnect is rationalized using equilibrium thermodynamics (phase diagrams) and diffusion kinetics. Manifestation of the Kirkendall effect accompanying reaction diffusion is elucidated by considering relative mobilities of species in the product phases.

Key words: low-temperature soldering, Transient Liquid Phase bonding, GaCu-alloy paste, Gallium, Copper, Silver, interfacial reactions.

INTRODUCTION
Soldering to heat- and stress-sensitive electronic devices, like, for example, Silicon-based photo multipliers, metallized piezoelectric materials with low Curie temperature, etc., is certainly not a simple straightforward procedure as it might look at first sight. Exposure to elevated temperature and thermo-mechanical stresses built upon cooling after bonding can profoundly affect overall performance of the electronic assembly. Obviously, to reduce this deleterious effect, soldering temperatures must be kept as low as possible.

In our previous contributions to the SMTA Conference [1, 2], it was suggested that low-melting Bismuth-Indium alloy containing 34 wt.% of Indium, which consists of ordered BiIn intermetallic-matrix and (Bi + BiIn)-eutectic, can, in principle, be used for soldering of heat-sensitive electronic devices and materials. The proposed ordered solder exhibits creep resistance and strength retention at high homologous temperatures. It was also shown that acetic acid vapor-phase (~118. 1 °C) soldering is worthy of serious consideration as a viable technique allowing for processing temperature control in fluxless soldering using the low-melting solder alloy.

Another practical approach to which a great deal of effort was directed is the use of Gallium-based materials. Low-melting Gallium-based alloys (melting point of Ga is 29.8 °C) attract special attention. These materials (or "pastes") can be malleable substances and can be produced by mixing (in suitable proportions) of, for example, Copper-powder and Gallium [1, 3-5]. (Note: Hereafter, the term "paste" is used to emphasize the simultaneous presence of Gallium-based melt and solid metal (e.g., Copper) powder in the original formulation at bonding temperature.) The Ga-based constituent in the paste can be consumed by the interfacial reactions with the powder (as well as with the substrate material) at temperature above its melting point resulting in a strong bonding to the substrate. This type of Transient Liquid Phase (TLP) bonding results in solidification (curing') of the alloy paste and allows for the joints to be fabricated at 120 °C, and the product assembly can be operational as high as up to ~ 200 °C. In fact, Ga-based pastes can be thought of as metallic adhesives, but upon cure they have electrical and thermal properties comparable to solder materials.

In the earlier publication [1], we demonstrated that through judicious selection of Ga- interlayer thickness between Cu-substrates, Transient Liquid-Phase (TLP) bonding can be achieved at temperatures just above melting point of Gallium,

and the resulting joints are capable of service at elevated temperatures. However, our attempts of using dendritic Cu-powders with average particle size 3 and 63 μm for soldering paste formulation by direct blending of metallic powder into liquid Gallium (with Cu to Ga ratio 1: 2), gave rather mixed results. It was found that although the Ga-based composite alloy wets Cu-substrate rather well and no voiding occurs at the substrate/composite solder interface, overall quality (and "reproducibility") of the alloy pastes appeared to be insufficient to recommend these materials for applications as low-temperature solder alloys.

One might expect that reproducibility of the solder material can be improved if spherical (instead of dendritic) Cu-powder (with a suitable particle size) is used for the paste formulation. It is also expected that reproducibility of the solder material can be improved further if both Cu and Ga in the alloy formulation are used in powder form. In such case, the solder alloy preparation can be accomplished by simple mixing of the constituents in solid state rather than by blending Cu-powder into liquid Gallium. Since no Gallium powder is commercially available, suitable pulverization techniques were developed.

The main objectives of the present investigation can be formulated as follows:

- To develop suitable pulverization technique(s) for Gallium.
- To formulate several soldering pastes from spherical Copper powder and Gallium with Ga to Cu ratios 1:2.
- Using equilibrium phase diagrams and diffusion kinetic data to elucidate reaction phenomena occurring during solidification (curing) of the newly formulated Ga-based alloy pastes on Cu- and Ag-substrates.
- To assess merits of using Ga-Cu alloys pastes for fabricating low-temperature solder interconnections.

For practical reasons as well as visual appreciation, the analysis of the reaction phenomena is presented here in rather simple terms and in a quite descriptive manner in order to convey it more graphically (and microstructurally) rather than attempting the formal treatment of the problem. However, this contribution is not a mere album of microstructures and in it are to be found interpretations of the underlying mechanisms governing morphological developments of the transition zones during the curing of the newly introduced alloys and fabrication of the solder interconnections.

EXPERIMENTAL PROCEDURES

Gallium (99.99 %), cold-rolled sheets and wires of Oxygen-free Copper (99.995 %) and Silver (99.95 %) as well as spherical Cu-powder (99.9 %) with a particle size in the range > 20 μm - < 70 μm were used as starting materials. The choice of Cu-powder was made in accordance with the estimations made in Ref. [5]. The authors concluded that for the case of the GaCu alloy paste containing 66 wt. % of Cu, the mean size of spherical particles of Cu should be no less than 6 μm.

Gallium-powder was produced by mechanical cryo-pulverization of the liquid metal in porcelain mortar using liquid Nitrogen and subsequent sieving to the fraction < 32 μm.

Several GaCu-solder alloys (with Cu-content 66 wt. %) were prepared either by mixing spherical Copper-powder and laboratory-made Ga-powder or by direct blending (manually or using a laboratory shaker) of Cu-powder into liquid Gallium at 70 °C.

The "freshly prepared" alloy pastes were applied (at 120 °C) on clean surfaces of Copper- or Silver- substrates and then cured (solidified) by being exposed to 120 °C for various periods of time ranging from 4 to 16 hours.

To "mimic" solder interconnect structure, the Cu-wire (300 μm or 800 μm) was positioned inside the initial alloy paste placed on the substrate. When Cu-substrates were used, in some cases, a small drop of hydrochloric acid was placed onto the substrate surface prior to the solder alloy application.

Heat-treatment (annealing) of the samples was conducted in a drying cabinet in air or under low vacuum (~ 0.05 bar). However, in most cases, annealing was performed on an electric hot plate. The processing temperature control was ±5 °C.

For investigation of reaction behavior in the Ag-Ga system, "sandwich" reaction couples Ag/Ga/Ag were prepared and exposed to (annealed at) 120 °C for 16 hours. The Gallium interlayer was introduced between the Ag-substrates directly from the melt at ~ 70 °C.

After visual inspection, sample cross-sections were made by direct grinding of the specimens embedded in transparent epoxy resin and subjected to standard metallographic preparation (usually grinding up to 4000 grit). Further, the sample cross-sections were examined first, by Optical, and then, by Scanning Electron Microscopy (SEM) and Electron-probe Microanalysis (EPMA) using Energy Dispersive X-ray Spectrometer (EDS). To improve electrical conductivity of the samples and make them suitable for electron-microscopic investigations, a thin layer of Carbon was deposited in vacuum on the metallographically prepared surfaces.

RESULTS AND DISCUSSION

Before starting with the demonstration and anticipating somewhat specific results of the present work, it seems worthwhile to recall some basic principles of Transient Liquid Phase (TLP) bonding technique and to explain its utilization in the Ga-based alloy paste design intended for joining at low-temperatures. This information will provide useful background and constitute natural introduction to the subject.

Transient Liquid Phase (TLP) Bonding - Basics

The basic principles of the Transient Liquid Phase (TLP) bonding process are shown schematically in Fig. 1 below.

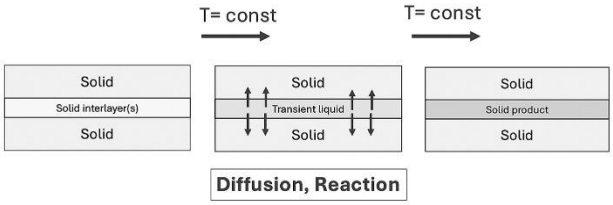
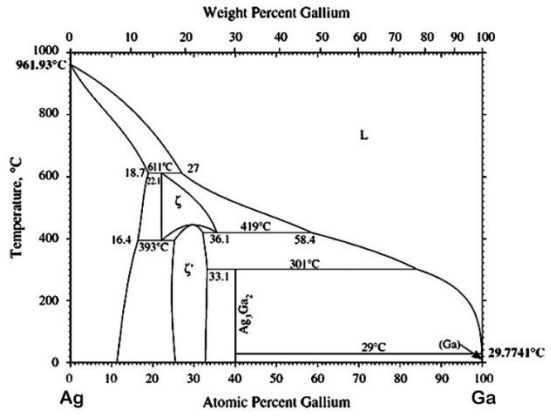


Figure 1. Schematic representation of the Transient Liquid Phase (TLP) bonding process.

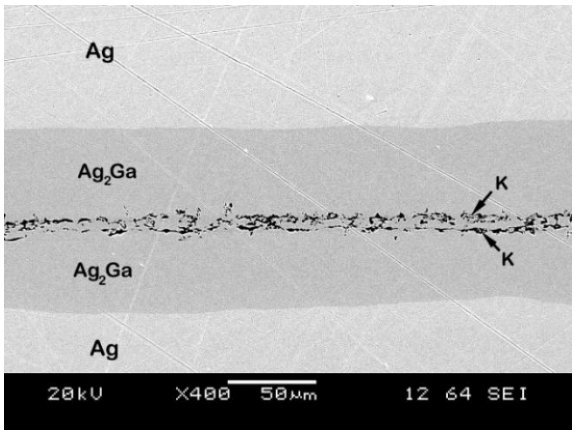
The interlayers in the joining assembly are designed to form a transient liquid phase to facilitate bonding via a soldering (or brazing)-like process in which the liquid disappears isothermally. In contrast to conventional soldering (brazing), the liquid disappears, and a higher melting point phase is formed at the bonding temperature. In fact, any system wherein a liquid phase disappears by diffusion, reaction (amalgamation), volatilization, or other processes is a candidate for TLP bonding. As already mentioned, the Transient Liquid Phase (TLP) joining process has a number of advantages compared to conventional soldering methods. Specifically, it enables the joining of materials and low temperatures and thereby preserves the properties and performance of temperature sensitive materials.

Gallium being low melting metal (its melting point is slightly above room temperature) is considered to be a good candidate for the interlayer material in low-temperature TLP bonding. It can wet most metallic surfaces found in microelectronic applications and inherently forms an instantaneous electrical and thermal contact [6].

A very telling example of using Ga-interlayer is provided by the fabrication of Ag-to-Ag joints. Interaction at the contact surface between liquid Gallium and solid Silver results in the formation of intermetallic compounds, which can be rationalized using latest version of the binary Ag-Ga phase diagram given in Fig. 2a [7].



a)



b)

Figure 2. The binary Ag-Ga phase diagram [7] in a) and b) Secondary Electron Image (SEI) of the reaction zone in the Ag-to-Ag joint fabricated by the TLP bonding technique using Gallium-interlayer (120 °C; 16 hours). Note. Letter K in b) indicates locations of the original liquid-solid contact surfaces ("Kirkendall planes").

A typical morphology of the reaction zone developed in "sandwich" Ag / Ga /Ag diffusion couple after exposure to 120 °C for 16 hours is shown in Fig. 2b. It can be seen that the reaction product layers in the diffusion zone are bound by the rather straight interfaces. It is remarkable that the formation of only ζ'-Ag_2Ga-intermetallic phase with large homogeneity range was observed in all reaction couples studied, and no Ga-rich stoichiometric compound Ag_3Ga_2, which exists in the Ag-Ga binary system was found. (Note: Hereafter, all intermetallic phases will be denoted in their binary formulae.)

It is possible that this phase is present in such a minute quantity that it cannot be detected by the experimental techniques used. However, given a finite configuration of the diffusion couple studied, it is also plausible that the "missing phase" Ag_3Ga_2, was consumed during interaction by the fast-growing Ag-rich (ζ'-Ag_2Ga) intermetallic.

Position(s) of the original contact interfaces (Kirkendall plane(s)) between the Ga-interlayer and Silver are revealed by the well-recognizable rows of pores originating from the surface defects (and perhaps, debris) that might be present at the initial Ag-surfaces. It is plausible that the apparent appearance of two Kirkendall planes inside the product interconnect is attributed to the fact that although Ga is by far the most mobile species in the ζ'-Ag_2Ga intermetallic, Ag also (intrinsically) diffuses through hexagonal (hP9) lattice of this phase [8]. This finding is worth mentioning here because the observed situation with the relative intrinsic diffusivities in the ζ'-Ag_2Ga product layer leads to the appearance of two distinct (stable) Kirkendall planes, i.e., they are not merged during interdiffusion inside the transition zone. The latter is very important from a technological point of view, since the Kirkendall plane is a notoriously problematic feature in the joint, because of higher mechanical failure risk at the (stable) Kirkendall plane.

The Gallium-based Alloy Paste

From a physico-chemical standpoint, the Ga-based alloy paste can be viewed as an "assembly" of large number of reaction interfaces formed between liquid Gallium and solid particles of the higher melting metal, and upon "curing", the liquid constituent of the paste is consumed by the interfacial reactions. The idealized microstructure developed in the paste and "hardness" profile (extent of the interaction) during curing is illustrated schematically in Fig. 3. Note. The "S-shaped" curve represents the typical kinetic behavior for most powder reactions [9].

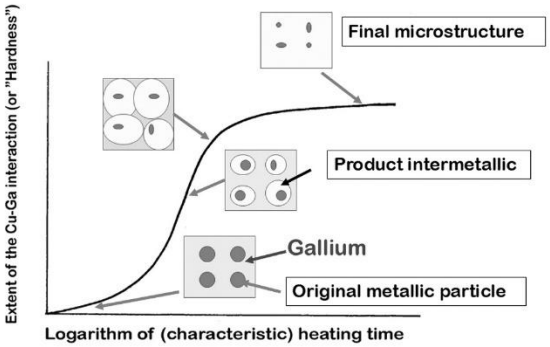


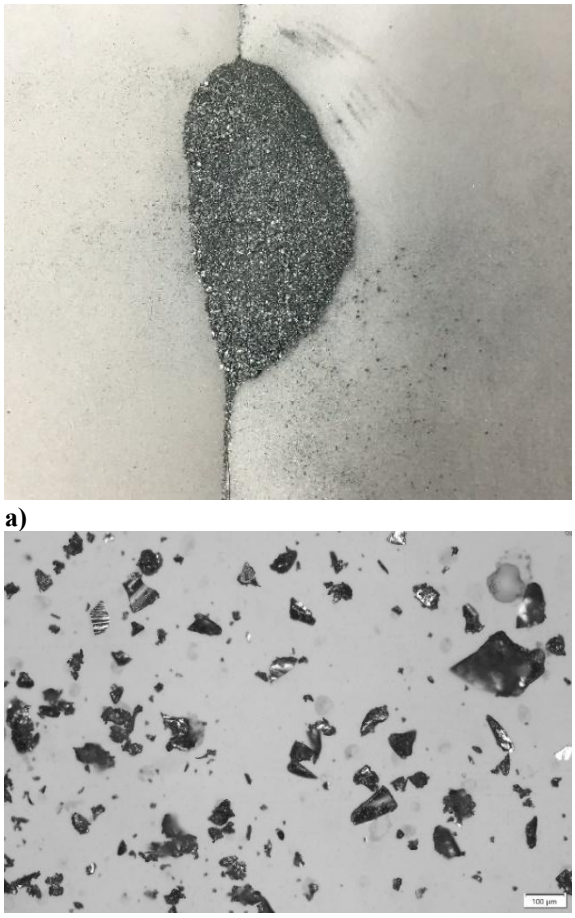
Figure 3. Schematic representation of the extent of interaction in (and hardness profile of) the mechanically alloyed Gallium + metallic powder mixture along with the corresponding evolution of the alloy microstructure during curing.

It is to be noted that quality of such diffusively solidified solder (and soldered joint) is determined largely by the capillary characteristics of the liquid phase, its ability to wet solid particles (and substrate), by melt-solid interaction features and by adhesion within the system. Obviously, the thickness of the Gallium-interlayer depends on the ratio of the components in the mixture (paste) and the specific surface area of the metallic powder. Time during which Gallium solders remain in a paste-like state and their curing (hardening) time are interrelated and depend on the specific surface area of the higher melting metal powder used in the alloy formulation. The lower the specific surface area of the metallic powder, the greater the thickness of the Ga-interlayer and the hardening (curing) time, and vice versa.

The ratio of constituents in the initial mixture (paste) and the powder particle shape and size mainly affect the mechanical properties of Gallium-based solder alloy. Increasing the amount of the higher melting metal powder, reducing the size of its particles, or changing their shape so that their specific surface area grows, will raise the mechanical strength, because the solidified (cured) solder alloy will have a finer microstructure. In addition, the finer the powder, the smaller the pores (voids) which may form during interaction between the alloy (paste) constituents and the better are the mechanical properties. However, as mentioned earlier, it was estimated that in the case of the GaCu66 alloy paste [5], the mean size of spherical particles of Cu should be no less than 6 μm.

Preparation of Gallium Powder for Soldering Paste Formulation

No Gallium powder is commercially available, and therefore, in the present work a special pulverization technique was developed. Gallium was mechanically pulverized under liquid Nitrogen. In this way, polydisperse flowable powder was obtained, which after cleaning in Aceton and drying in air can be stored at sub-ambient temperature (Fig. 4).

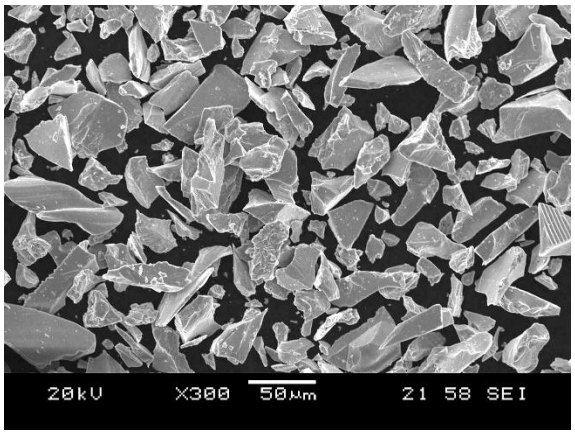


a)

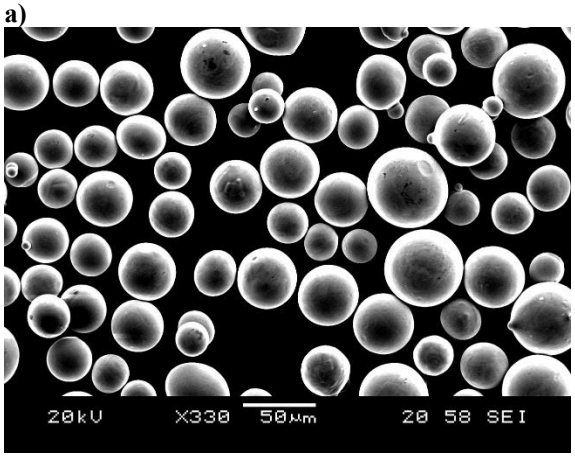
b)

Figure 4. Gallium powder produced by (mechanical) cryo-pulverization of Gallium under liquid Nitrogen: a) general view of the flowable powder and b) bright-field optical image showing polydisperse nature of the powder and acicular morphology of the particles.

After pulverization procedure, the product powder was sieved first, to fraction < 90 μm, and then, down to fraction < 32 μm. Typical morphology of the Ga-powder in the fraction < 32 μm is shown in Fig. 5a. Note. The brittle nature of the fracture occurring during cryo-pulverization of Gallium is evidenced by the acicular shape and sharp edges of the particles (Fig. **5a**).



a)



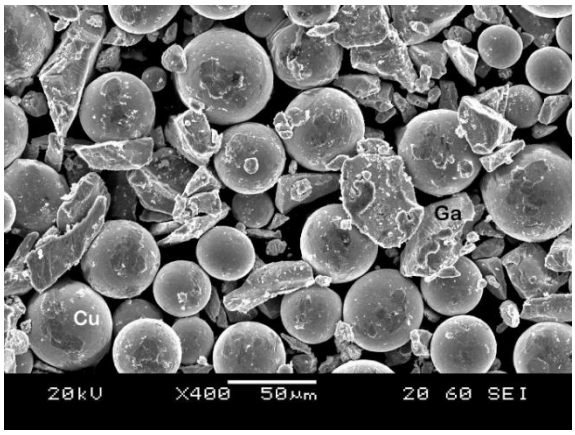
b)

Figure 5. SEIs showing morphology of a) the laboratory made Ga-powder sieved to the fraction < 32 µm together with b) spherical Cu-powder (> 20 µm - < 70 µm) used for the soldering paste formulation.

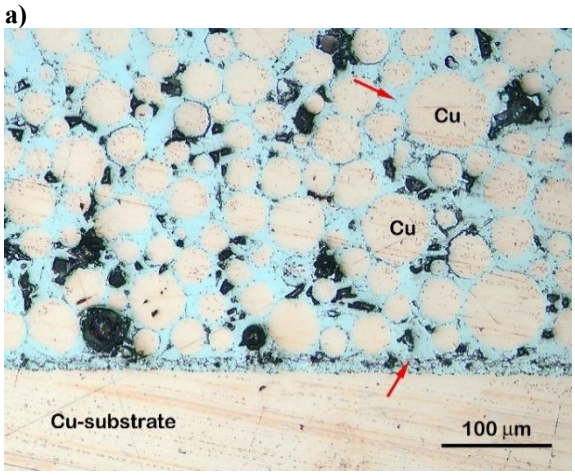
Further, for the soldering paste formulation, the Ga-powder of the fraction < 32 µm is mixed (manually or using a laboratory shaker) with spherical Cu-powder with the particle size > 20 µm - < 70 µm (Fig. **5b**).

Curing of Ga-Cu Composite Solder Alloy on Copper Substrates

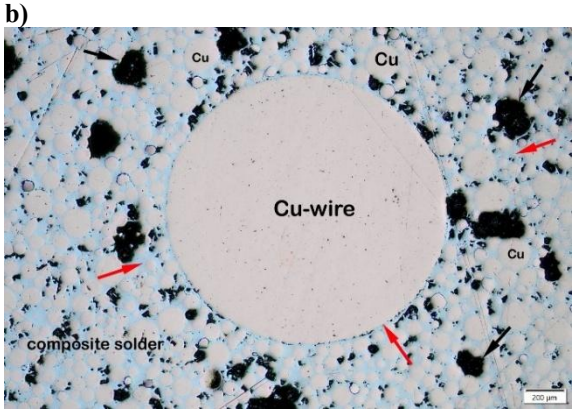
Morphology of the "as-prepared" GaCu solder alloy containing 34 wt. % of Gallium produced at room temperature by manual mixing Ga-and Cu-powders with particle size < 32 µm and > 20 µm - < 70 µm, respectively is presented in Fig. **6a** below. As expected, after mechanical mixing of the constituent powders, some Gallium was found on the surface of the Cu-particles and Oxygen was detected (in terms of the EPMA/EDS) on the surface of the Ga-particles.



a)



b)



c)

Figure 6. A montage of microphotographs showing: a) morphology (SEI) of the "as-prepared" GaCu-solder alloy containing 34 wt. % of Gallium produced at room temperature by manual mixing Ga-and Cu-powders with particle size < 32 µm and > 20 µm - < 70 µm, respectively together with bright-field optical images of the sample cross-section taken from the Cu-to-Cu interconnect fabricated at 120 °C for 16 hours in air using the GaCu66 alloy paste: b) obtained in the vicinity of the Cu-substrate and c) recorded in the vicinity of the Cu-wire. Note. Red arrows in b) and c) indicate locations of the product $CuGa_2$ intermetallic.

After application of the "freshly prepared" powder alloy on the Cu-substrate at 70 °C and positioning of 800 µm Cu-wire into the solder paste followed by the exposure at 120 °C in

air for 16 hours, the Gallium constituent was found to be converted into $CuGa_2$ intermetallic, and the resulting interconnect microstructure contains numerous voids (**Fig. 6b, 6c**).

According to the binary Cu-Ga phase diagram shown in Fig. 7 [10], interaction between Gallium and Copper at 120 °C under equilibrium conditions should result in the formation of several intermetallic phases. However, only one, tetragonal (tP3) $CuGa_2$-intermetallic compound was found in the fabricated interconnect. Following line of arguments explained before for the case of interaction in the Ag / Ga / Ag couples, it is very possible that the Cu-rich phases are present in such a small quantity that they cannot be detected by the available analytical techniques.

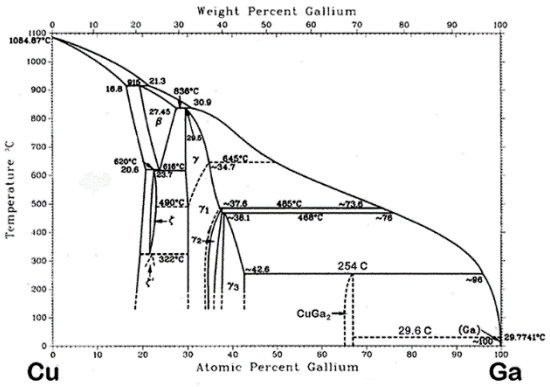
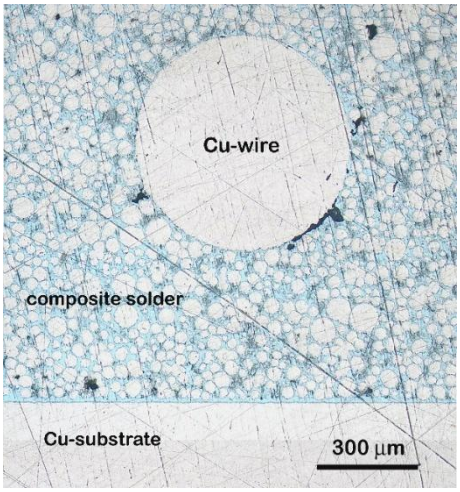
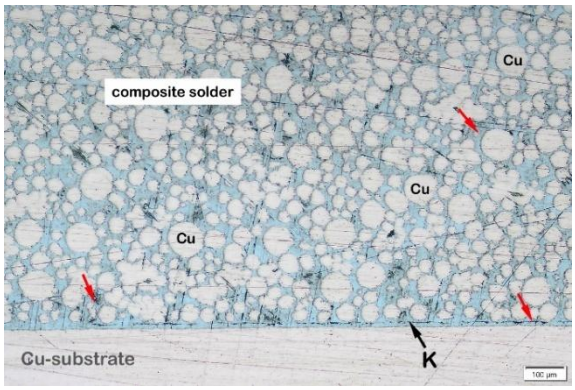


Figure 7. The binary Cu-Ga phase diagram [10].

When GaCu66 alloy paste fabricated by blending Cu-powder with particle size > 20 µm - < 70 µm into liquid Gallium at ~70 °C was used for manufacturing Cu-to-Cu joints (120 °C; 16 hours; air), the phase composition of the product interconnect was found to be the same as in the solder joint described above. The liquid (Ga) constituent of the alloy paste was consumed entirely by the reaction with Cu and good bonding across the contact surface with Cu-substrate as well as with the Cu-wire was achieved.



a)



b)

Figure 8. Cross-section of the Cu-to-Cu joint soldered in air at 120 °C for 16 hours with GaCu66 alloy paste fabricated by blending Cu-powder (particle size > 20 µm - < 70 µm) into liquid Gallium at ~70 °C: a) general view and b) magnified area of the sample cross-section revealing position of the Kirkendall plane in the vicinity of the composite solder/Cu-substrate interface (indicated by letter K). Locations of the $CuGa_2$ phase formed during fabrication of the solder interconnection are indicated by red arrows in (b). Note the unfortunate artefact (the presence of scratches) in (a) which stems from the metallographic preparation of the cross-sectional sample.

However, in contrast to the case of using GaCu66 alloy paste prepared from the solid powders, no notable voiding was observed inside the Cu-to-Cu interconnect after exposure to similar experimental conditions.

Another important microstructural feature that should be noticed from the micrograph shown in Fig. **8b** is the location of the Kirkendall plane. The latter is revealed by the row of "natural" inert markers (pores originated from the surface defects, grinding debris, etc.) within the product $CuGa_2$ phase layer adjoined to the Cu-substrate, but not at the interphase interface, which, as mentioned earlier, it is very critical to the overall performance of the solder interconnect: the Kirkendall plane is a weak spot in any joint.

Diffusion mechanisms in the Cu-Ga intermetallic phases are not established at present, although it is generally accepted that substitutional migration of atoms in the intermetallic compounds occurs by virtue of vacancy-type defects [11]. In the absence of clearly defined operative mechanisms, any attempt at understanding the diffusion process will obviously involve possible correlations between the behavior of these specific compounds and their crystal structure.

The $CuGa_2$-phase has a tetragonal (tP3) $FeSi_2$-type crystal structure which can be viewed as a defect superlattice derived from the CsCl-structure [8]. Based on experimental observations, it may be concluded that in such cell arrangement both components, Ga and Cu can diffuse in the lattice of $CuGa_2$ intermetallic.

Curing of Ga-Cu Composite Solder Alloy on Silver Substrates

Interaction of the composite GaCu66 alloy fabricated by blending Cu-powder (particle size > 20 µm - < 70 µm) into liquid Gallium at ~70 °C during diffusional solidification on Ag-substrate at 120 °C in air for 16 hours resulted in the joint morphology presented in Fig. 9a.

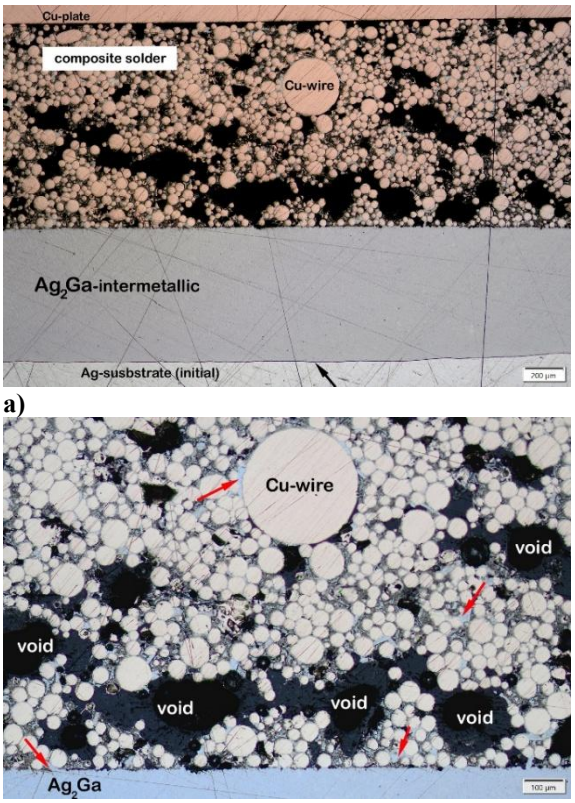


Figure 9. Bright-field optical images of the GaCu66 composite solder alloy fabricated by blending Cu-powder (particle size > 20 µm - < 70 µm) into liquid Gallium at 70 °C after curing (in air) on Ag-substrate at 120 °C for 16 hours: a) general view revealing a distinct boundary between the intermetallic product layer and remains of the initial Ag-substrate (indicated by arrow in (a) together with b) magnifies area of the sample in the vicinity of the solder alloy/Ag_2Ga-product layer interface showing the presence of $CuGa_2$-product phase inside the composite alloy (indicated by red arrows in (b). Note. To "mimic" interconnect structure, a (300 µm) Cu-wire was introduced into the solder alloy prior exposure to the soldering temperature, and Cu-plate was placed on the "drop" of the solder (a).

From the micrographs, it is immediately apparent that during curing of the paste with the same Ga to Cu ratio (1: 2) on Ag-substrate, reaction of the liquid (Ga) constituent with the substrate is much faster than that observed during hardening on Cu-substrates (cf. Fig. 8). These very fast kinetics of the reaction between Silver and liquid Gallium results in a heavy wicking of the liquid constituent from the GaCu-alloy paste leading to significant voiding inside the interconnect structure.

Again, as in the case of the Ag/Ga/Ag diffusion couple (Fig. **2b**), only layer of Ag_2Ga intermetallic was formed, and no Ga-rich phase Ag_3Ga_2 was detected inside the reaction zone. It is, of course, possible that this phase is present in such a minute quantity that it cannot be detected by SEM/EPMA.

Close inspection of the reaction zone in the vicinity of the reaction product / Ag-substrate interface revealed the formation of peculiar periodic layered morphology consisting of more or less regularly spaced layers (bands) of particles (containing Oxygen) embedded in a matrix phase of the Ag_2Ga reaction product (Fig. 10).

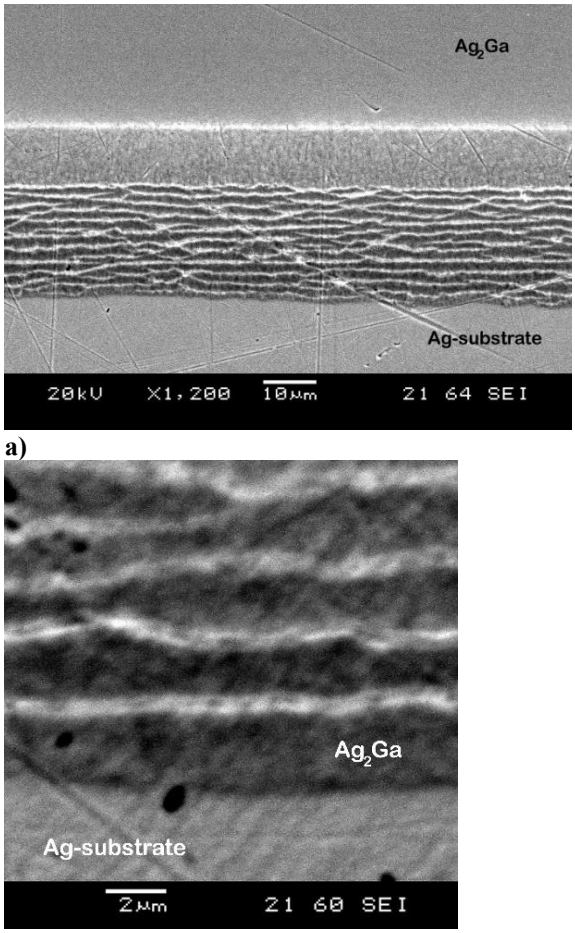


Figure 10. SEIs of the reaction zone developed in the vicinity of the Ag-substrate/reaction product interface (indicated by arrow in Fig. 9) showing the developed periodic layered morphology: a) general view and b) magnified area of the interfacial region reveling two-phase structure of the constituent bands within the periodic pattern, exhibiting light contrast in the SEI.

It is well documented [12] that internal precipitation reactions in some dilute binary and ternary alloys can be periodic in space and time, quite analogous to the Liesegang phenomenon. In displacement solid-state reactions, on the other hand, another mechanism responsible for the formation of reaction zone morphologies periodic (in time and space)

was accepted, which is related to manifestations of the Kirkendall effect accompanying interdiffusion in the solid state. The patterning during multiphase diffusion is attributed to diverging vacancy fluxes within the interaction zone. This can generate multiple Kirkendall planes, which by attracting in situ-formed inclusions of 'secondary-formed phase' can result in a highly patterned microstructure.

However, in the case at hand, we are dealing with the patterned microstructure of a different origin. It was found that one of the constituents of the periodic layered structures is a band of particles containing Oxygen which is not a component in the material system studied! It is conjectured that appearance of the periodic (in space and time) layered morphology during curing of the GaCu-alloy paste on Ag-substrate can be connected with the high thermodynamic stability of Ga_2O_3 which is invariably present on the surface of Gallium (liquid or solid). If a continuous layer of this protective surface oxide is damaged, it will be healed in air (by oxidation).

The Ga_2O_3 is 'chemically inert' with respect to the metallic constituents of the material system under consideration. Therefore, the remnants of the surface oxide layer which may be disintegrated during paste application by, for example, shapeshifting or agitation of the liquid constituent of the GaCu-alloy paste in contact with the Ag-substrate, may act as 'fiducial markers' marking location of the liquid metal surfaces.

The Ga-based liquid 'free of the surface oxide' reacts at the Ag-substrate resulting in the formation of the ζ'-Ag_2Ga compound, and further growth of the intermetallic layer (i.e., propagation of the reaction) will require diffusional transport of the reacting species through the product phase.

It was observed that at 120 °C, Gallium is the most mobile species in the non-stochiometric ζ'-Ag_2Ga intermetallic, although Ag was also found to diffuse (intrinsically) in the lattice of this phase (see Fig. 2b). It is well-known [13] that inert microscopic inclusions can migrate in the diffusion zone due to the imbalance of vacancy fluxes. In the present case, because of the large difference in intrinsic mobilities of species in the ζ'-Ag_2Ga, growth of the product phase layer will be accompanied by movement (shifting) of the oxide inclusions towards the contact surface with the GaCu-alloy.

When, for whatever reason, the intimate contact between liquid Ga and product phase in some domains of the interphase interface is compromised, the oxide layer will form instantly on the liquid Gallium surface at these specific locations creating a 'diffusion barrier' for Ga, while in other domains, diffusional growth of the ζ'-Ag_2Ga intermetallic will be uninterrupted. Apparently, the 'freshly' formed oxide layer on the surface of the Gallium-based liquid may also be damaged by the shapeshifting and intermetallic growth will proceed at these locations as well. Again, remnants of the disintegrated surface oxide layer will act as 'fiducial markers' marking position of the liquid metal contact surfaces. The processes described will continue as long as shapeshifting of the liquid metal, which damages the 'freshly' formed surface oxide layer on the Gallium-based melt, may occur, providing that the liquid Ga-alloy is available for the interaction.

CONCLUSIONS

Based on the results of the present work the following conclusions can be drawn:

- Flowable powder of Gallium can be prepared by mechanical cryo-pulverization under liquid Nitrogen and the product powder can be sieved to the fraction < 32 μm.
- Gallium-Copper solder alloys with Cu-content 66 wt. % can readily be formulated at room temperature by mixing commercially available spherical Copper-powder (particle size > 20 μm - < 70 μm) and the laboratory made Ga-powder with average particle size < 32 μm.
- The Ga-Cu alloy paste with the same Ga to Cu ratio can also be made by blending at 70 °C (manually or using laboratory shaker) the commercially available spherical Copper powder (> 20 μm - < 70 μm) into liquid Gallium.
- The newly developed GaCu-alloy pastes can be used for manufacturing Copper-to-Copper joints at temperatures below 120 °C, which are expected to be operational at higher temperatures.
- Transient Liquid Phase (TLP) bonding technique using Ga-interlayer can be employed for joining Ag-substrates at 120 °C and, again, the product interconnection can be operated at significantly higher temperatures.
- The GaCu-alloy pastes can, in principle, be used for joining Ag-substrates as well, but the very fast kinetics observed in the reaction of Silver with liquid Gallium results in a heavy wicking of the liquid (Gallium) constituent from the GaCu-alloy paste.

FUTURE WORK

The future is, of course, infinitely open, and we have every reason to believe that the proposed approach and materials introduced are of importance for the systems where low temperature fluxless soldering is paramount. At present, several recommendations for future work can be made:

- Mechanical testing of the Copper-to-Copper interconnections fabricated at 120°C with GaCu66 alloy paste should be conducted at higher temperatures.
- The detrimental effect of the oxide film present on the surface Ga-particles on quality of the GaCu66 alloy paste as well as voiding in the product solder interconnect can be reduced by compacting (prior to the use as a solder) of the manually prepared mixture of Copper-powder (particle size > 20 μm - < 70 μm) and the laboratory-made Ga-powder with average particle size < 32 μm. Perhaps, compaction of the powder mixture should be accomplished by pressing at sub-ambient temperature.
- A certain sort of 'reaction barrier' is necessary between the Ag surface and the Ga-based alloy paste, and, in this

case, Nickel or Ni(P) can be a good candidate as barrier material.

- On the other hand, to improve adhesion at the Cu / CuGa-alloy contact surface during soldering, a thin layer of Silver can be deposited on the Cu-substrate surface.
- Given the fact that in some places on Earth, outside temperature may exceed melting point of Gallium, i.e., 29.8 °C, storage of the Ga-powder can be an issue. Perhaps, another metallic component in the solder paste formulation with higher melting (liquidus) temperatures than that of Gallium should be found. In this respect, ternary Sn-In-Bi eutectic alloy with composition 16 at. % Sn; 30 at. % Bi; 54 at. % In and melting point ~58 °C (Fig. 11[14]) can be a suitable candidate.

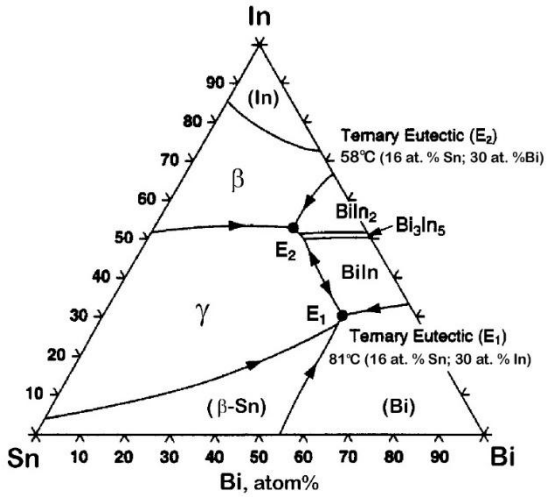


Fig. 11: Liquidus projection in the Sn-Bi-In system [14].

- Application of vapor phase soldering method with its unique ability of processing temperature control [15] is worthy of serious consideration as a viable technique for low-temperature, fluxless soldering below 120 °C.

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