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EXPRESS REGULAR ARTICLE

Hybrid Interconnection Process Using Solderable ICAs (Isotropic Conductive Adhesives) with Low-Melting-Point Alloy Fillers

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In order to overcome several crucial limitations to the traditional electrically conductive adhesive bonding used in the electronics field, a novel low-melting-point alloy (LMPA)-filled ICA (Isotropic Conductive Adhesive) was synthesized. Also, a hybrid interconnection process using it was developed, which can be achieved by melting-coalescence-wetting behavior of LMPA fillers in ICA. In order to ensure excellent coalescence and wetting characteristics of the LMPA filler particles, the fluxing capability of the resin should have been sufficient to remove the oxide layer on the surfaces of the filler particles and the electrode materials. The effect of reductant on the hybrid interconnection formation was examined.

ICAs with and without reductant were formulated with a 40% volume fraction of filler. The QFP chip had a size of 14 × 14 × 2.7 mm and a 1 mm lead pitch. The test board had a 18 µm thick Cu daisy-chained pattern. Thermal characteristic of the ICA was observed by differential scanning calorimetry (DSC), and the temperature-dependant viscosity characteristic of the polymer matrix was observed by torsional parallel rheometer. Based on the results, the reflow profile of the interconnection process was determined. The dipping interconnection method was applied in the QFP bonding process. After the QFP bonding process, the electrical characteristic of ICA was measured with a multimeter. The wetting, bondability, coalescence characteristics of the LMPA filler particles and the morphology of the conduction path were observed by microfocus X-ray inspection systems and optical microscopy. As a result, the LMPA-filled ICAs with reductant had stable contact resistance, forming the metallurgical interconnection. A good electrical conduction path was achieved with the coalescence and wetting characteristics of the molten solder particles in the ICA. [doi:10.2320/matertrans.M2009109]

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1. Introduction

Sn-Pb eutectic solder has been widely used in the electronics packaging industry as a material to bond electronic parts onto PCBs (Printed Circuit Boards). It provides excellent performance, quality, mechanical and electrical characteristics, and pitch capability. However, due to the toxicity problems in the Sn-Pb eutectic solder and international environmental regulations, research to develop alternative solder materials, such as Pb-free solder[1)] and electrically conductive adhesives (ECAs),[2,3)] have been actively investigated.

ECAs consist mainly of a polymer matrix and conductive particles. ECAs can be processed at a lower temperature than common solder, with superior thermal fatigue characteristics. They are environmentally friendly because they use a lead-free alloy. Their use is simpler overall because they do not require flux or a cleaning process.[4,5)]

Isotropic conductive adhesives (ICAs), one of the ECAs, have an all-directional electricity flow. Due to its all-directional conduction characteristics, ICAs can be applied selectively to the pad and heated. As a result of the shrinkage caused from polymer curing, it forms a conductive path through the physical/mechanical contact of conduction particles within the polymer.[6)] However, compared to metallurgical interconnections, this kind of bonding has low electrical and heat conduction capability, unstable contact resistance, low impact and joint strength, and Ag migration problems.[7–9)]

In this study, in order to solve the problems of traditional ICAs, a new concept of ICAs with low-melting-point alloy (LMPA) is proposed. By combining the merits of soldering and ICA bonding techniques, a new hybrid interconnection process was developed. In addition, Quad Flat Package (QFP) bonding was done using the newly developed ICAs. The electrical and mechanical characteristics for the newly developed ICAs are confirmed by measuring the electric resistance and mechanical strength of completely interconnected QFPs. In addition, we have observed the morphology of the conduction path between the QFP lead and the substrate formed by melting-coalescence-wetting behavior of the LMPA fillers in ICA.

2. Hybrid Interconnection Process Using Solderable ICA

Figure 1 shows a schematic of the hybrid interconnection mechanism using solderable ICA. Solderable ICA mainly consists of LMPA fillers and polymer matrix with reduction capability against oxide films of conduction pads and LMPA fillers. The polymer matrix has a reducing agent with an inherent reduction capability represented by the formula $R(COOH)_x$ (x is larger than or equal to 2). During the reflow process, the viscosity slowly decreased due to the chemical reaction of the polymer matrix. The organic carboxylic acid in polymer matrix removes the oxide layer on both the surface of the particle and the conductive pad according to following reaction formula.

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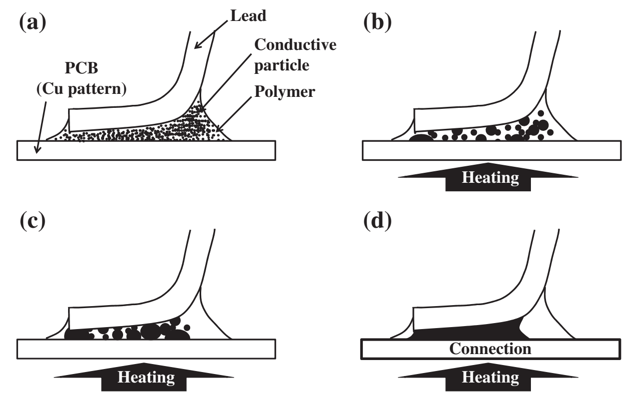

Fig. 1 A schematic of the hybrid interconnection mechanism using solderable ICA. (a) Initial condition, (b) and (c) coalescence and wetting behavior of LMPA fillers, and (d) completion of the hybrid interconnection process using solderable ICA with LMPA fillers.

$$\mathrm{mR{-}\underset{\overset{\|}{O}}{C}{-}O{-}H} \;+\; [\mathbf{MeO}] \longrightarrow \mathrm{mR{-}\underset{\overset{\|}{O}}{C}{-}O{-}}[\mathbf{Me}] \;+\; \mathrm{nH{-}O{-}H} \qquad (1)$$

The water generated during the chemical reaction between carboxylic acid and the oxidation layers is used by the amide hydrolysis for epoxy curing. Therefore the void formation due to the generated water can be restrained.[10] As the temperature reached the melting point of the LMPA filler, the reduced fillers melt, coalesce with each other, and grow to form a large spherical blob. Also, the reduced fillers connected with nearby molten fillers, and wetted on the upper and lower conduction pads. Finally, an electrical conduction path is formed between the upper and lower conduction pads as a result of the excellent coalescence and wetting behaviors of the reduced molten filler.

Using this hybrid interconnection mechanism, the hybrid interconnection process using solderable ICAs and QFP package was developed as shown in Fig. 2. This process combines the merits of the soldering and adhesive bonding methods; such as the metallurgical bonding of soldering and low temperature ICA bonding process. At first, solderable ICAs with LMPA filler were selectively applied on the QFP leads using a dipping method. After the QFP was mounted onto the PCB electrode pads, the test assembly was reflowed. The interconnection mechanism is metallurgical bonding due to the melting, coalescence, and wetting behaviors of LMPA fillers in ICA. This is quite different from the conventional ICA bonding mechanism of physical/mechanical contacts of filler materials.

3. Experimental

3.1 Materials

In this study, ICAs with and without reductant were formulated with a 40% volume fraction of filler. Diglycidylether bisphenol A (DGEBA), which is a thermosetting resin, was used as the binder. Diaminodiphenyl sulfone (DDS) was used as a curing agent, and an amine type catalyst was used. Carboxylic acid was used to remove the oxide layer from the surfaces of the LMPA fillers and the conduction pad.

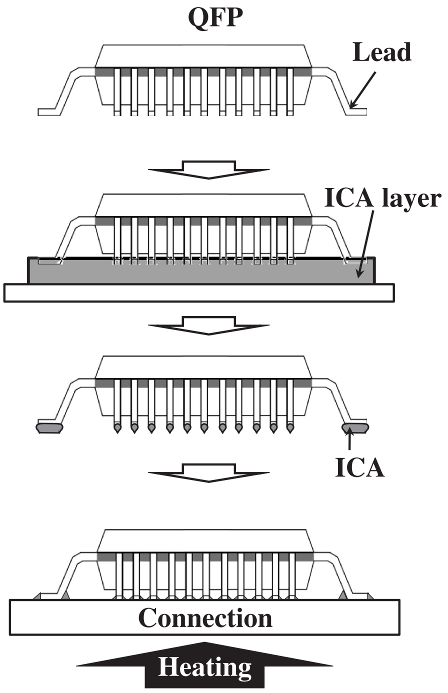

Fig. 2 A schematic of hybrid interconnection process using solderable ICA and QFP package.

Table 1 Components of new formulation of ICA.

Components	
Epoxy	DGEBA
Curing Agent	DDS
Catalyst	Amine type
Reductant	Carboxylic Acid
LMPA Filler	Sn-58Bi ($\varphi 45\,\mu m$)

The selected LMPA filler in the polymer matrix was Sn-58Bi from Senju Metal Co., which has a relatively low melting temperature of 412 K and higher ultimate strength and shear strength comparing those of Sn-37Pb eutectic alloy. The materials formulating the ICAs are shown in Table 1, and the configuration of the QFP used in the test is shown in Fig. 3.

The QFP was 14 × 14 × 2.7 mm in size and had a 1.0 mm lead pitch. It had 44-pin I/O terminals plated with Sn. The pattern of the PCB was plated with a 18 μm thick Cu, and the QFP and PCB pattern were daisy-chained in order to measure the electrical resistance.

3.2 Test method

3.2.1 Differential scanning calorimetry (DSC) and viscosity test

Differential Scanning Calorimetry (DSC) was used to measure the curing behavior of the polymer and the melting behavior of the LMPA fillers. Thermodynamic analysis was carried out. In order to observe the temperature-dependant viscosity characteristics of the polymer, a viscosity test was carried out using a torsional parallel rheometer.

For DSC analysis, a sample was put in the DSC pan under an air-purged, nitrogen gas environment. The heating rate was 10 K/min. Its temperature was raised from room temperature to 573 K to observe the changes in heat flow.

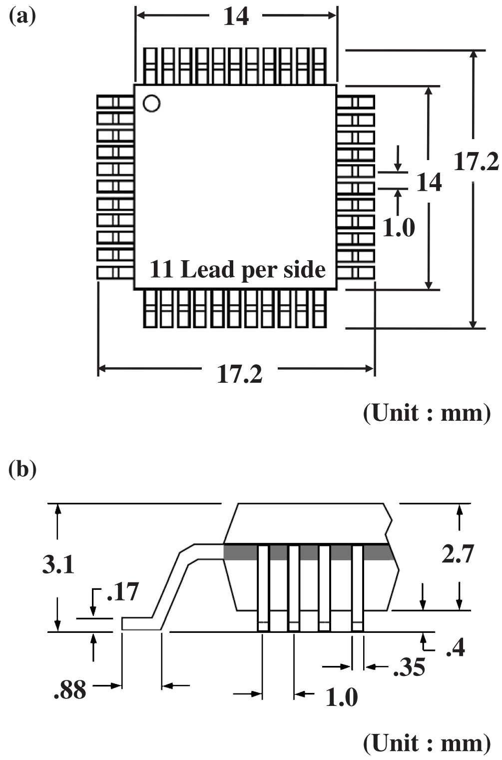

Fig. 3 Configuration of QFP. (a) Top view and (b) side view.

In order to measure the behavior of the polymer and LMPA fillers, each sample was measured individually. For the viscosity test, the polymer matrix was put on a 20 mm diameter plate. Using a 1 Hz frequency, the heating rate was the same as in DSC test. The matrix temperature was raised from room temperature to 523 K and the changes in the viscosity of the polymer were measured.

Through the results from DSC analysis, the temperature profile for the interconnection process was determined.

3.2.2 Wetting test

In order to investigate whether the polymer matrix can provide reduction capability, LMPA wetting test was performed. A copper patterned test board was used. The test boards were cleaned by ultrasonic cleaning with acetone for 1 min. Then, they were rinsed with DI water and dried with an air jet. A LMPA solder ball with a diameter of 750 µm was placed on the metallization. Then an amount of polymer matrix was applied to cover the ball. The test board was heated with the temperature profile. The reflowed test board was then cross-sectioned using polisher, and the wetting angle was measured using an optical microscope (VHX-100: KEYENCE Co.).

3.2.3 Hybrid interconnection test

A hybrid interconnection test was carried out for five specimens using the newly developed ICAs and QFP package. The hybrid interconnection test was as follows. The substrate test boards were cleaned with acetone for 1 min. Then they were washed with DI water and dried with an air-jet. The volume fraction of the LMPA in formulating ICAs with and without reductant was 40%. To apply the ICAs onto the QFP leads, a flat ICA layer was previously formed on the flat glass substrate using a squeegee method. After the complete formation of the ICA layer, the lead part of the QFP was dipped into the ICA layer to ensure that ICAs were selectively applied on the QFP leads. After completion of the QFP and substrate alignment, QFP was mounted on the PCB electrode pads using the flip chip bonder (LAMBDA: FINETECH Co.). Then, the test assembly was heated according to the temperature profile determined from the DSC analysis and viscosity test. After the QFP interconnection was completed, the electrical resistance was measured through a daisy-chain connected probe terminal. The bonding condition of the LMPA fillers in the polymer was also inspected, using an X-ray inspection system (SMX-160: Shimadzu). The morphology of the conduction path that was formed through the wetting and coalescence behavior in the QFP interconnection was observed with an optical microscope (VHX-100: KEYENCE Co.).

In order to confirm their electrical characteristics, the total electrical resistance of their interconnection was measured. The lead wire of the multimeter (34410A: Agilent Technologies) was attached to the probe terminal connected daisy-chain of the interconnection completed PCB and measured. For the bondability of hybrid interconnection, the 45 degree pull test (JIS Z 3198-6) on QFP lead was performed. The QFP lead was pulled upward at 6 mm/min and total number of leads pull tested was 22 for each of ICAs with and without reductant.

4. Results and Discussion

4.1 Materials characterization

The results of the DSC analyses of the curing behavior of the polymer and the melting behavior of the LMPA fillers, as well as the results of the viscosity test of the polymer matrix, are shown in Fig. 4. The curing peak temperature of the polymer was 427.41 K and endothermic peak of Sn-58Bi was 414.34 K. This result meant that polymer curing did not occur around the melting point of the LMPA filler. Also, as can be seen from the polymer viscosity test results, at a temperature range slightly higher than the melting point of the LMPA filler, the polymer matrix maintained a very low viscosity (about 100 cPs).

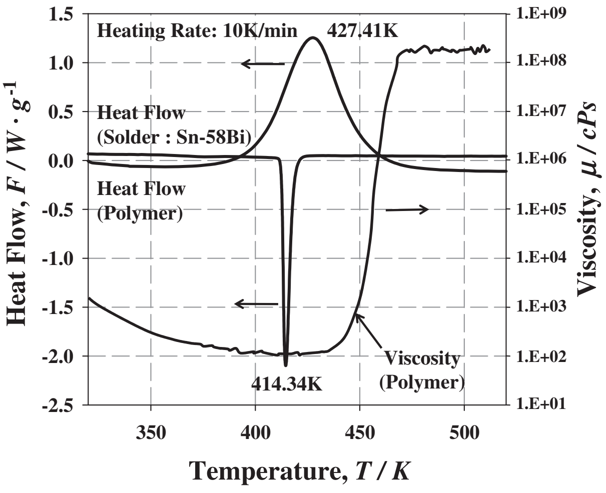

Fig. 4 Dynamic DSC and DMA scan at 10 K/min for the polymer matrix and LMPA filler.

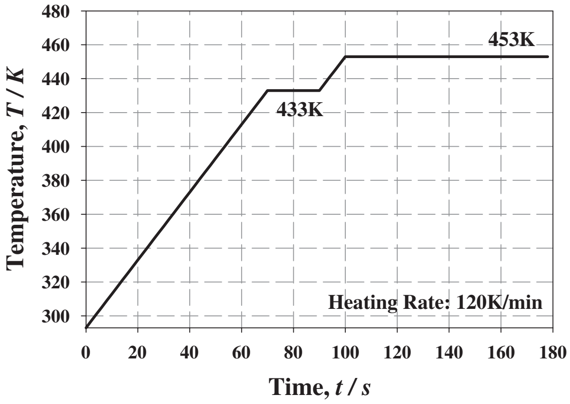

Fig. 5 Temperature profile for the QFP bonding process using solderable ICA.

The polymer should not be cured too much before it reaches the melting point of the LMPA filler in order to achieve a good electrical conduction path. Thus, melted LMPA fillers in ICA are flowed more easily, coalesced with nearby fillers, and wetted on the QFP leads and PCB conduction pads during the interconnection process. Excessive curing of the polymer hinders the flow, coalescence, and wetting behaviors of LMPA fillers in ICA and will ultimately inhibit achieving the good electrical conduction path.

The temperature profile for the QFP interconnection process was determined through the results of DSC analysis and a viscosity test as shown in Fig. 5. The temperature profile was divided into the soldering stage (for the melting, flow, coalescence, and wetting behaviors of the LMPA filler in ICA) and the curing stage (for the completeness of bonding achieved by curing of polymer).

In the soldering stage, the test vehicle was heated at a ramped heating rate of 120 K/min to 433 K and maintained 433 K for 20 s, which was 20 K higher than the melting point of the LMPA filler (412 K), in order to ensure complete melting of the LMPA fillers. In this stage, a conductive path start to be formed by the melting, flow, coalescence, and wetting behaviors of the LMPA fillers in ICA. After it had successfully passed the soldering stage, it was heated to 453 K at 120 K/min, and maintained for 80 s in order for complete curing of the polymer. After curing was completed, the conductive path had been fixed by the curing shrinkage, resulting in increased mechanical strength.

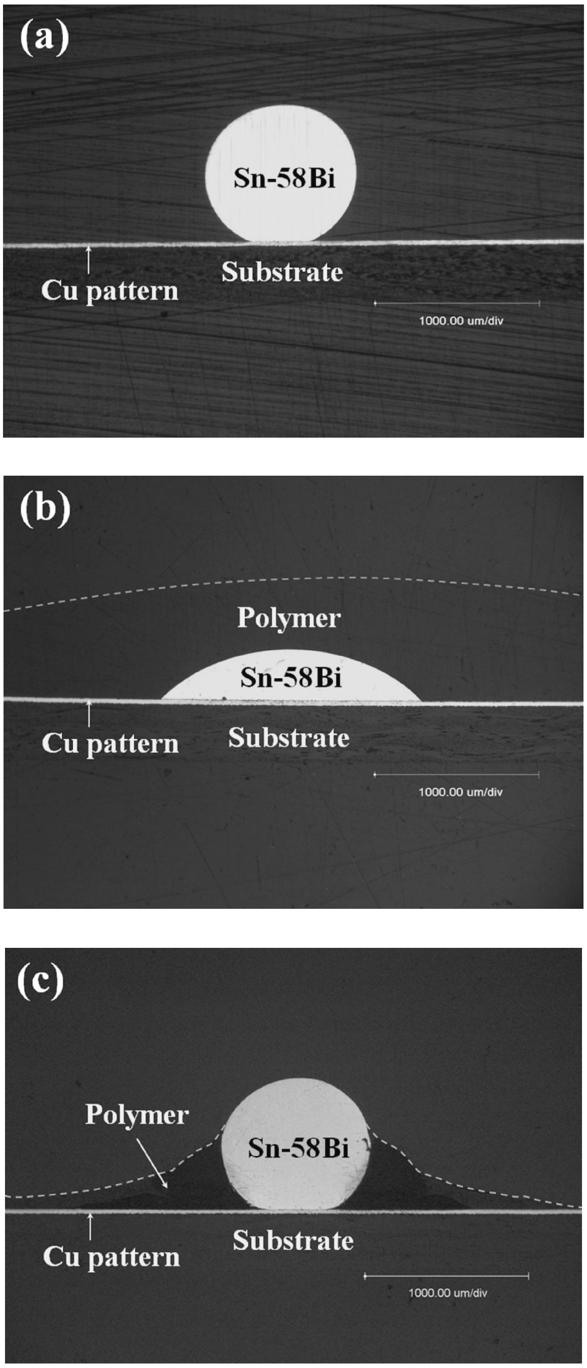

Fig. 6 Wetting morphology of LMPA (a) without ICA, and in ICAs (b) with reductant, and (c) without reductant.

4.2 Wetting test

In order to realize good coalescence and wetting of the LMPA filler, the organic carboxylic acid must be added to the epoxy resin. The carboxylic acid removes the oxide layer on both the surface of the particle and the conductive pad in accordance with previously mentioned hybrid interconnection mechanism. Specifically, this organic carboxylic acid should be chemically compatible with the epoxy resin without any gas being produced during the bonding process.[11)]

Figure 6 shows the wetting morphology of eutectic Sn/Bi LMPA on Cu metallization. As shown in the results, the wetting angle of solder ball on Cu without ICA was about 160 deg and it was about 34 deg for ICA with reductant. On the other hand, it was about 160 deg for ICA without reductant, which is almost same level comparing with that of case without ICA. These results indicated that the ICA with reductant has an excellent wetting characteristic due to the fluxing capability against the oxide layer on the surfaces of the filler particles and the electrode materials.

4.3 Hybrid interconnection process

Figure 7 shows the X-ray photographs of the QFP assembly after the hybrid interconnection process using solderable ICAs. In the figure, the LMPA fillers that fill the area between QFP lead and PCB conduction pad are shown in the dark gray region. The polymer-filled area is shown in

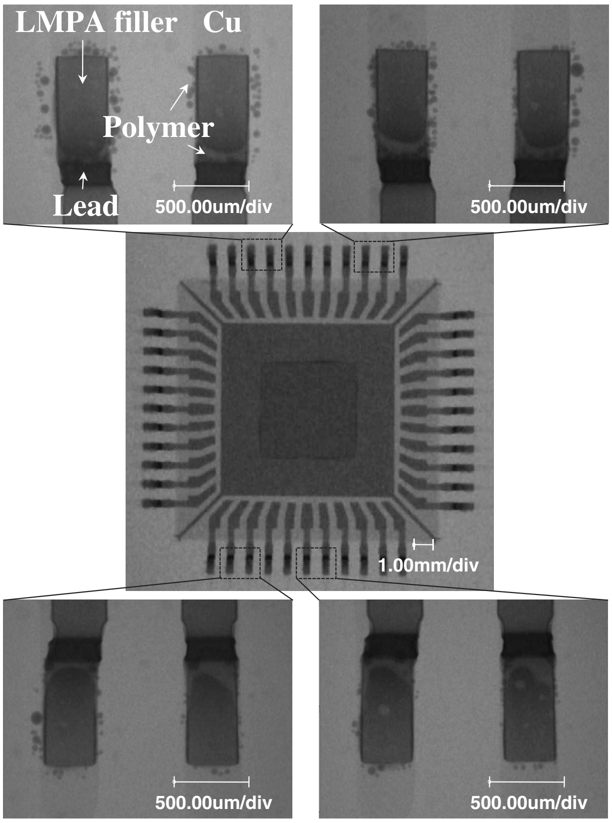

Fig. 7 X-ray photographs of the QFP assembly with solderable ICA with reductant.

the light gray region. In the dark-gray area, with the coalescence and wetting behaviors of the melted LMPA fillers in ICA, the QFP lead was covered evenly forming a stable conductive path. The dark gray dots on the outside of the facing QFP lead and PCB conduction pad area are LMPA fillers that were melted and coalesced with nearby LMPA fillers, but, remained unwetted because they were not sufficiently flowed and wetted on both QFP lead and PCB conduction pad. Though fillers that did not participate in interconnection existed in the polymer region of the outside pattern, the amount was very small in quantity, and existed near the pattern. Also, they were covered with the polymer so that their insulating properties were retained.

Figure 8 shows the morphology of the conduction path of the completed QFP interconnection. The bonded parts are divided into two definite regions. One part is a conductive path made by melted fillers that metallurgically interconnected QFP lead and PCB conduction pad. The other part is polymer wrapped around the conduction path on the outside, and attached the lead and substrate. The dotted line shows the cured polymer region of the exterior of the interconnection. In previous studies,[12–14)] it has been shown that the fluxing capability of the ICA to remove oxides of both LMPA fillers and conduction pads is one of the essential conditions for achieving the stable metallurgical conduction path. Also, we reported that two different types of conduction paths (necking type and bump type) in the ICA formulations, corresponding to the epoxy matrix, were formed by the wetting and coalescence behaviors of the LMPA fillers. As for the epoxy matrix without reduction capability, the necking-type conductive path was formed by uniting of the melted fillers at the high filler loading ($V_f \geqq 50\%$). The presence of the surface oxide films on both filler and metallization pads caused the fillers to form a network, rather than fully coalesce into a homogeneous mass during the curing process. It was because the oxide films were destroyed only at the contact area, the melted fillers got wet locally, and the necking-type conductive path was formed. As for the epoxy matrix with reduction capability, on the other hand, the bump-type conductive path was formed by reduced LMPA fillers even though the filler loading volume fraction was low ($V_f = 30\%$).

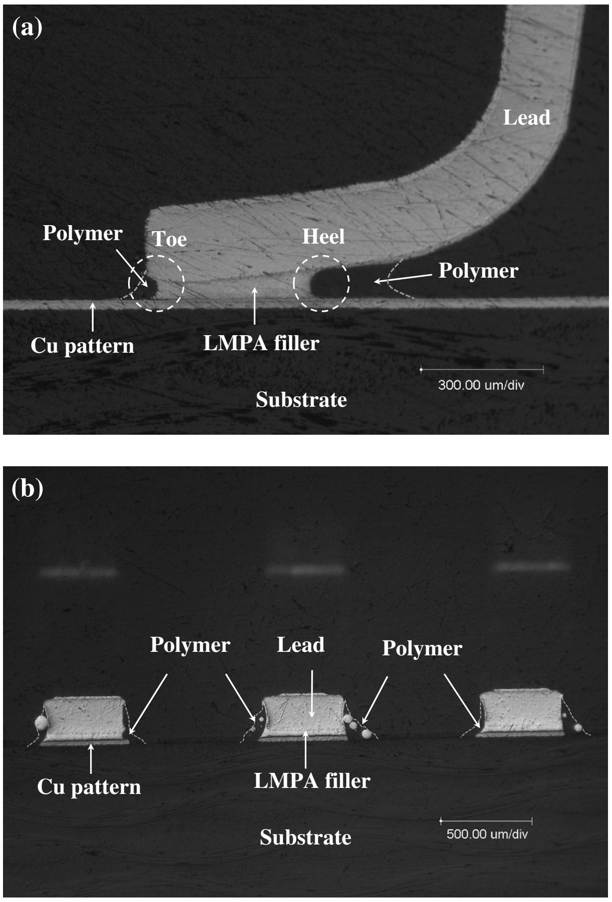

Fig. 8 Morphology of the conduction path between QFP lead and PCB conduction pad of the substrate for ICA with reductant. (a) Side view and (b) front view.

As seen in the figure, newly developed ICA has a good fluxing capability. LMPA fillers form an enormous, ball-shaped filler and then collects between the lead and electrode pad because of the coalescence and wetting behaviors of the melting filler, as well as by capillary force. At the same time, the viscosity-decreased polymer flows out and cures, and then forms the final part of the interconnection. It cannot be observed any voids due to the solvent and bubbles. The void can be formed by the entrapped air during polymer matrix preparation, the solvent to control the viscosity of polymer matrix and the bubbles. The bubbles may be created by the unreacted acids such as methacrylic acid and 3-butenoicacid and further the water also generated bubble during the chemical reaction between carboxylic

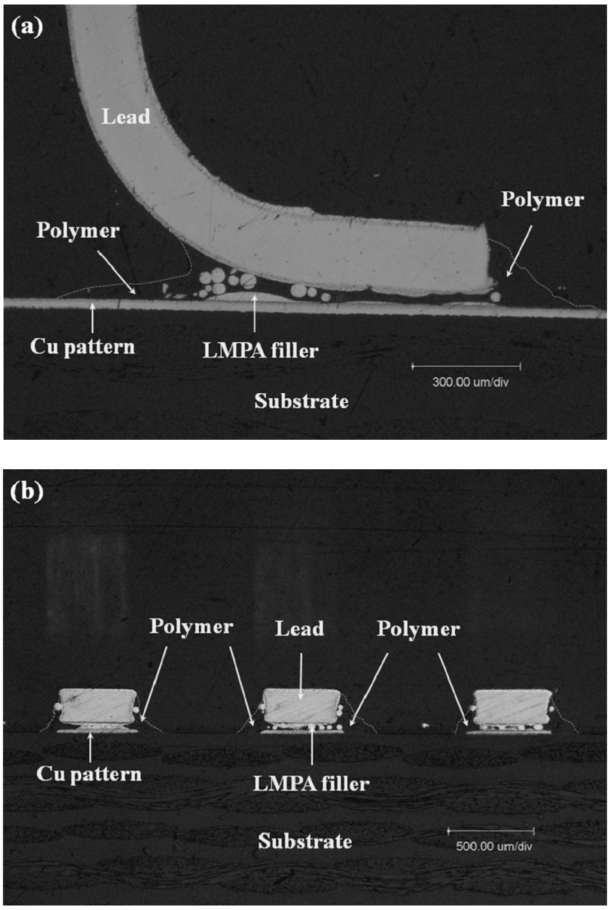

Fig. 9 Morphology of the conduction path between QFP lead and PCB conduction pad of the substrate for ICA without reductant. (a) Side view and (b) front view.

acid and the oxidation layer on the LMPA filler surface. Therefore, the carboxylic acid should be carefully prepared using a minimum amount of solvent and the solvent should be removed during ICA preparation before the bonding process.

As seen in the Fig. 8(a), the toe and heel of the QFP interconnection part can be formed by the wetting of the solder. It can be known that active wetting behavior occurred because of the fluxing capability of the polymer during the interconnection process. In addition, as can be seen in Fig. 8(b), a good conduction path was observed for all the interconnection parts of the QFP. The polymer wrapped well around the lead part of the polymer and the outside of the conduction path. Additionally, the existing fillers on the outside that did not contribute to the wetting behavior on the inner side of the polymer covered the outer side of the interconnection part, thus preventing short circuits near terminals.

On the other hand, the metallurgical interconnection could not be achieved when using ICA without reductant. As shown in Fig. 9, LMPA fillers were not almost wetted on the upper and lower pads and coalesced with each other. The spherical LMPA fillers remained between QFP lead and electrode pad, because the remained oxide layers on the surfaces of the filler particles and the electrodes hindered the wetting and coalescence characteristics in ICA.

Table 2 Electrical resistance of QFP interconnection for ICAs with and w/o reductant.

	ICAs	Test Number of QFP chip				
		1	2	3	4	5
Electrical Resistance [Ω]	ICA with reductant	1.919	2.041	2.059	2.047	1.955
	ICA w/o reductant			∞		

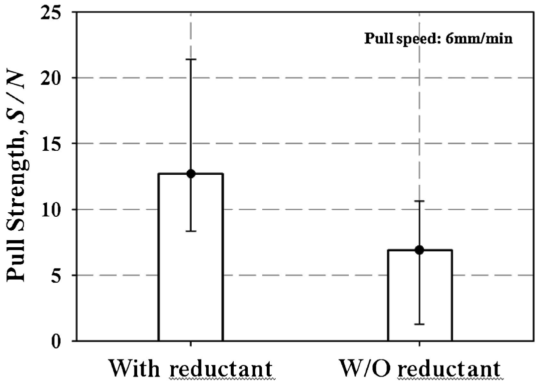

Fig. 10 Pull strength of the QFP leads for ICAs with and without reductant.

Table 2 shows the total electrical resistance of each test vehicle. By forming an electrical conduction path with a metallurgical interconnection, the solderable ICA-based interconnection was stable, and acquired excellent electrical characteristics. The average total electrical resistance was $2 \pm 0.063\,\Omega$. On the other hand, in case of QFP interconnection formed by using ICA without reductant, a stable electrical characteristic could not obtain because no metallurgical interconnections were formed. These results showed that the QFP interconnection with solderable ICA contained reductant has a good electrical property due to the metallurgical interconnection formed by the coalesced and wetted LMPA fillers rather than by the physical/mechanical bonding method of traditional ICAs. In the hybrid interconnection process using the solderable ICA, ICA facilitates the wetting and coalescence characteristics of the LMPA fillers to form a stable metallurgical network for electrical conduction while also forming an ICA joint providing adhesion like a conventional ICA process.

Figure 10 shows the pull strength of the QFP leads for ICAs with and without reductant. On the QFP interconnection with solderable ICA contained reductant, they exhibited good strength properties. It can be seen that the pull strength measured for the ICA with reductant was comparable to that of solder. This is due to the robust interconnection achieved through the metallurgical bonding between the QFP leads and electrodes. The pull strength was 8.35 N to 21.39 N and average pull strength was 12.71 N, which was about twice higher pull strength compared with that of the QFP leads for ICA without reductant.

5. Conclusion

In this study, we developed a new class of solderable ICA using a polymer with a fluxing capability and LMPA fillers.

Also, a new hybrid interconnection process using solderable ICAs, that combines the merits of the soldering and adhesive bonding techniques, have been developed.

The results show that the developed polymer matrix has an effective fluxing capability on the candidate LMPA filler and electrode. Also, the melted LMPA fillers in ICA formed stable conduction paths between QFP lead and PCB conduction pad through a melting, coalescence, and wetting behaviors. Also, the QFP interconnection with solderable ICA with reductant had good electrical and mechanical characteristics, due to the metallurgical interconnection formed by the coalesced and wetted LMPA fillers. It could be enhanced the electrical resistance instability problems resulting from the traditional ICA bonding method, which formed electrical conduction path by the mechanical/physical contact of fillers. In addition, its application should be possible not only for QFP bonding process but also for BGA, CSP, and flip chip bonding using solderable ICAs.

Acknowledgements

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