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Reliability Enhancement of Anisotropic Conductive Adhesives Flip Chip on Organic Substrates by Non-Conducting Filler Additions

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Abstract: Flip chip assembly on organic substrates using ACAs have received much attentions due to many advantages such as easier processing, good electrical performance, lower cost, and low temperature processing compatible with organic substrates. ACAs are generally composed of epoxy polymer resin and small amount of conductive fillers (less than 10 wt.%). As a result, ACAs have almost the same CTE values as an epoxy material itself which are higher than conventional underfill materials which contains lots of fillers. Therefore, it is necessary to lower the CTE value of ACAs to obtain more reliable flip chip assembly on organic substrates using ACAs. To modify the ACA composite materials with some amount of conductive fillers, non-conductive fillers were incorporated into ACAs.

In this paper, we investigated the effect of fillers on the thermo-mechanical properties of modified ACA composite materials and the reliability of flip chip assembly on organic substrates using modified ACA composite materials.

For the characterization of modified ACAs composites with different content of non-conducting fillers, dynamic scanning calorimeter (DSC), and thermo-gravimetric analyzer (TGA), dynamic mechanical analyzer (DMA), and thermo-mechanical analyzer (TMA) were utilized. As the non-conducting filler content increased, CTE values decreased and storage modulus at room temperature increased. In addition, the increase in the content of filler brought about the increase of Tg^{DSC} and Tg^{TMA}. However, the TGA behaviors stayed almost the same.

Contact resistance changes were measured during reliability tests such as thermal cycling, high humidity and temperature, and high temperature at dry condition. It was observed that reliability results were significantly affected by CTEs of ACA materials especially at the thermal cycling test. Results showed that flip chip assembly using modified ACA composites with lower CTEs and higher modulus by loading non-conducting fillers exhibited better contact resistance behavior than conventional ACAs without non-conducting fillers.

1. Introduction

As the improvement of electronic devices proceeds on, the electronic packaging technology trends move toward lower cost, finer pitch, higher electrical performance, and better reliability. As a result, flip chip technology gains popularity as one of the best chip packaging candidates to meet these trends.

Although flip chip assembly using solder balls is in the main stream of flip chip technology, flip chip assembly using conductive adhesives such as isotropic conductive adhesives (ICAs) and anisotropic conductive adhesives (ACAs) has been under development because of their potential advantages compared with soldered bumps.[1)~4)] Some advantages of ACA flip chip assembly are (1) lower processing temperature (epoxy curing less than 150°C compared with 240°C solder reflowing temperature), (2) finer pitch interconnect (less than 50 μm pitch achieved at chip on glass (COG) technology), (3) lower cost due to

less processing steps, and (4) green process (no lead, fluxes, and cleaning solvents).

ACAs, basically composite materials composed of an adhesive polymer resin and conductive particles, such as metallic or metal-coated polymer particles, have brought much attentions as an alternative for flip-chip-chip on organic boards.

For the full implementation of flip chip using ACAs, it is necessary to provide good reliability data to prove the availability of ACAs flip chip technology. The most commonly observed flip chip failure is during the thermal cycling test, which is due to the thermal expansion mismatch between chips and substrates. Therefore, underfill materials with matched coefficient of thermal expansions (CTEs) between chips and substrates are needed to guarantee better reliability. However, underfill materials can not be used for ACA flip chips, because chips are attached to substrates using ACAs. Therefore, the problem of CTE mismatch between chips and substrates becomes serious with the ACAs flip chip assembly because of high CTE of ACAs materials. For this reason, we have patented the new dielectric filler added ACAs which function not only electrical interconnection but also the underfill function at the same time.[5] Our previous study showed that low CTE adhesive layer with high filler content had lower shear strain induced by CTE mismatch between the chip and the board under temperature cycling.[6]

The purpose of this study is to investigate the effect of added dielectric fillers on ACAs materials characteristics such as dynamic mechanical, thermo-mechanical, and rheological properties, and reliability of modified ACA flip chip on organic boards applications.

2. Experiments

To investigate the reliability of ACA flip chip assemblies, three ACA composites with different filler contents were formulated, and materials properties were tested. The effect of various ACAs on the reliability of ACA flip chip on organic boards was measured using thermal cycling test.

2-1. Materials

Silica fillers of different content (5-45 wt.%) and nickel fillers were mixed with liquid epoxy to produce ACAs of 10 wt.%, 30 wt.% and 50 wt.% total filler content. Surface modification of fillers was performed to get uniform dispersion of filler inside epoxy matrix of ACA composite. The ACA were formulated by mixing fillers, liquid epoxy resin, and a hardener. The mixtures were stirred and degassed under a vacuum for 3 hours to eliminate the air induced during stirring. The differential scanning calorimeter (DSC) was performed to investigate curing properties of ACA composites. The cured ACA samples were prepared by placing the adhesive mixture in a convection oven at 150°C for 30 min and cutting with 0.6 mm thick dimension for the thermo-mechanical characterization such as dynamic mechanical analysis (DMA), thermogravitational analysis (TGA) and thermo-mechanical analysis (TMA) test. The uncured ACA solutions were also prepared to interconnect flip chip on organic substrates.

2-2. Characterization

2-2-1. Differential scanning calorimeter (DSC)

DSC experiments were carried out to determine the curing profile and the glass transition temperature (Tg) of ACA materials with different filler contents using modulated DSC instrument (by TA Instruments, Model 2920). Aluminum pans containing 7~8 mg ACA materials were heated from 25°C to 250°C at a heating rate of 10°C/min under nitrogen condition to determine the curing profile of the ACA composite samples. Next the samples were cooled down to 25°C slowly and heated again up to 200°C at the same heating rate to determine Tg of the cured ACA samples.

2-2-2. Dynamic Mechanical Analysis (DMA)

The storage modulus and loss modulus measurement of cured ACA composite samples were performed on DMA instrument (by TA Instruments, Model 2980) to investigate the effect of filler content on the modulus of cured ACAs. DMA test specimens were prepared by placing a liquid formulation of ACA composite into an aluminum pan (37.5 mm diameter). And then the specimen was preheated in an 80°C convection oven followed by heating up to 150°C with 10°C/min heating rate and curing in the oven at 150°C for 5 min. After that, the sample was removed from the oven, cooled

down to room temperature, and cut into square with dimensions of about 2×11×35 mm. The measurement was performed in single cantilever mode under 1 Hz sinusoidal strain loading. Storage modulus (E') and loss modulus (E'') were calculated by the preinstalled software.

2-2-3. Thermo-Mechanical Analysis (TMA)

The CTE measurement of cured ACA composite samples with different filler contents was performed using TMA instrument (by TA Instrument, Model 2940). The preparation of a specimen used for TMA testing was the same as for the DMA testing. But the specimen size for TMA testing is 5×5×2 mm. A sample placed on the TMA sample cell was heated from 20°C to 150°C using a heating rate of 5°C/min. The CTEs were obtained from the amount of thermal expansion versus temperature.

2-2-4. ThermoGravitational Analysis (TGA)

The thermal stability of cured ACAs was investigated by measuring deterioration temperature and weight loss using TGA instrument (by TA Instruments, Model 2050). A sample of cured ACA composites was placed into a platinum TGA sample pan, and then heated in TGA furnace from 25°C to 500°C with a heating rate of 10°C/min under N_2 purging (77 ml/min in vertical direction and 12 ml/min in horizontal direction). A curve of weight loss versus temperature was then obtained. The onset temperature of the weight loss step was defined as the initial temperature of the decomposition of the cured sample.

2-3. Bump Formation

2-3-1 Gold Stud Bump Formation

It is necessary to form bumps on the I/Os of the chip to be interconnected on the substrate using ACA materials. The gold stud bumps were formed on each I/O pad of test chips using a modified wire bonding machine. First, as in conventional wire bonding, a gold wire was bonded to the chip I/O pads by thermo-compression and ultrasonic energy. Next, the capillary tube clamping the wire was withdrawn and the wire was cut. And then, stud bumps were coined by pressing against a flat surface to make bumps height uniform. Fig. 1(a) shows coined stud bumps formed on aluminum I/Os of test chip.

Fig. 1(a). Scanning electron microscopy of coined Au stud bumps formed on Al pads of test chip.

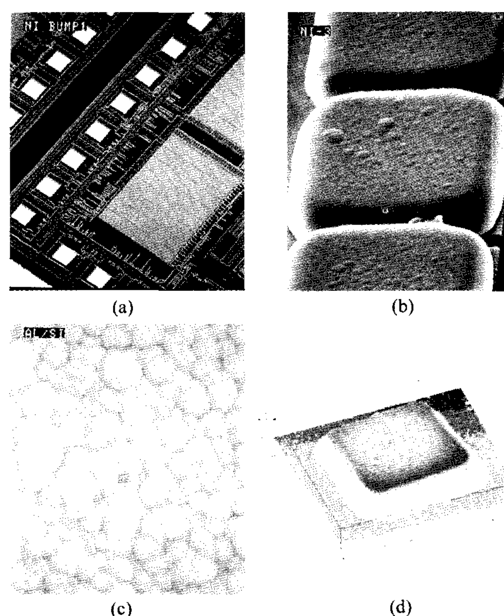

Fig. 1(b). Electroless Ni Bumps (a) unbumped Si chip, (b) Ni bumps, (c) surface morphology, and (d) configuration of Ni/Au bump.

2-3-2 Electroless Ni Bump Formation

The electroless bumping process is wet-chemical and maskless (Kloeser, J., 1998). Test chips with 5 mm×5 mm size were processed with an Al layer thickness of 1 μm and a passivation layer of 0.5 μm silicon nitride. The passivation openings of the bond pads are 75 μm and pad pitch is 150 μm. The processing steps are: (1) zincate treatment on Al I/O pad surface. Al surface

Table 1. Specification of test chip and organic substrate

Specification	Substrate
Material	FR-4
Size (mmxmm)	34×37
Final metallization	Au
Specification	**Test IC**
Size (mmxmm)	5×5
I/Os	48
Pitch (μm)	130
Pad size (μm diameter)	60
Bumps	Au stud bumps Electroless Ni bumps

should be activated to plate Ni because Ni is not electroless plated on Al surface. However, in this process Al is dissolved by the zincate solution. (2) Electroless Ni plating-mushroom shape electroless Ni bumps with 20 μm height were formed in sodium hypophosphite plating bath at 90°C for 1 hour. (3) Final gold flash with 0.05 μm thickness was applied to the electroplated Ni surface for preventing oxidation. Fig. 1(b) shows Al pad in the test chip, electroless plated Ni bumps and surface morphology.

2-4. Flip Chip Assembly using ACA

The modified ACAs in this study consist of an insulating epoxy thermosetting adhesive, conductive fillers, and non-conductive fillers. The modified ACAs were adhesive pastes without solvent. The substrate used for flip chip assembly was 1 mm-thick FR-4 board. The specifications of test chip and test board are summarized in Table 1.

There are three process steps for the ACA flip chip assembly on an organic substrate. First, the gold stud bumps on the chip and the I/O pads on the test substrates were aligned. And then the ACA was dispensed on the substrate to interconnect the chip. Finally, bonding pressure of 2~3 kgf/cm^2 and temperature of 150°C for 5 min was applied to bond the chip on the substrate. Thus the chip is electrically connected to the substrate via entrapped conductive fillers of the ACA. Non-conductive fillers with smaller diameter than conductive fillers do not contribute the electrical contacts. Fig. 2 shows schematic of flip chip bonding process using ACA and the appearance of chip on an organic FR-4 substrate using an ACA composite material.

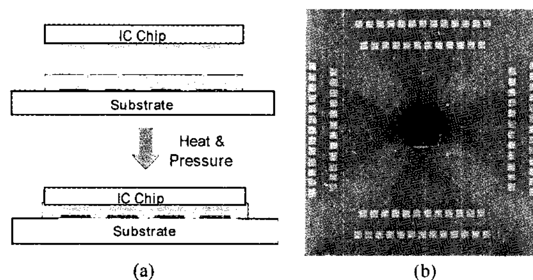

Fig. 2. (a) Schematic of flip chip bonding process using ACA and (b) the appearance of flip chip assembly on an organic substrate such as FR-4 using an ACA composite material.

2-5. Reliability Test

To investigate the reliability of ACAs flip chips on an organic substrate, contact resistance of a single interconnect is the most important characteristic. The initial contact resistance was measured using a 4-point probe method and after each time interval, in-situ contact resistance were measured during the completion of reliability tests. For the reliability test conditions, 85°C/85%RH high humidity and temperature condition for 1000 hours, 85°C/dry high temperature/dry condition for 1000 hours, and 60°C to 150°C air to air thermal cycling for 700 cycles condition were adapted.

3. Results and Discussion

3-1. Material Characterization

3-1-1 DSC results

The DSC curves in Fig. 3 show the effect of filler contents on the curing profiles of ACA composite materials. Similar curing behaviors and glass transition temperature of three different ACA composite materials were observed. However, the increase in the filler content slightly shifted the curing onset temperature and peak temperature to the higher temperature as shown in Fig. 3(a). The addition of nickel and silica fillers slightly modified the shape of the DSC curves and increased the Tg. The increase of Tg by addition of fillers has been known as general phenomenon.[6]

3-1-2. DMA results

The dynamic mechanical properties of ACA

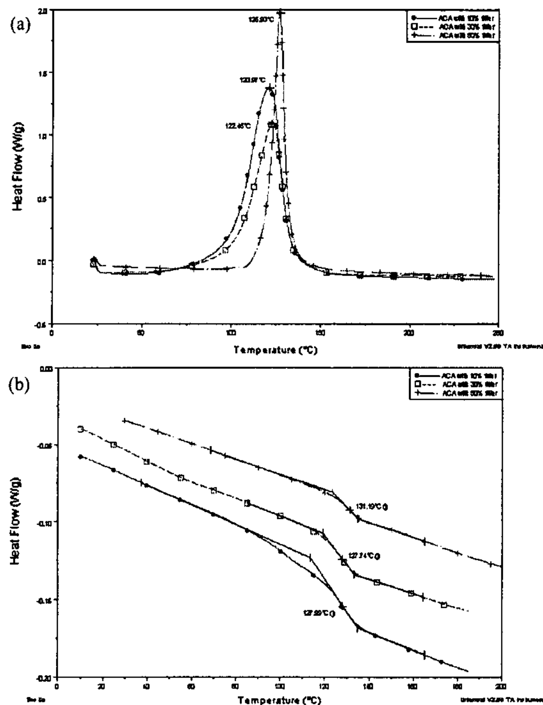

Fig. 3. DSC curves of ACA samples with nickel and silica fillers of different contents (10, 30, 50 wt.%) Effect of the filler contents on (a) the curing profiles and (b) the glass transition curves of three ACA composites.

composites from room temperature to 200°C were studied using DMA. The Fig. 4 shows the variation of the storage (E') and loss (E") modulus as a function of the temperature for the ACA composites with different filler contents. The modulus of the ACA materials, particularly the storage modulus, increased as the content of silica increased at room temperature and decreased as the temperaure increased. Fig. 4 shows that the glass transition temperature characterized by a knee in the E' curves and the maximum in the E" curves increase as filler contents increase. These behavior can be due to the increased interactions of polymer/filler in ACA composites. The composites will acquire some increase in free volume when fillers are filled into the matrix materials. If the filler content is increased continually, the internal friction due to increase of polymer/filler interface will rise quickly, hindering the movement of the polymer molecules even though the free volume of the composite increases. This increase in friction resulted in a higher value for Tg as filler

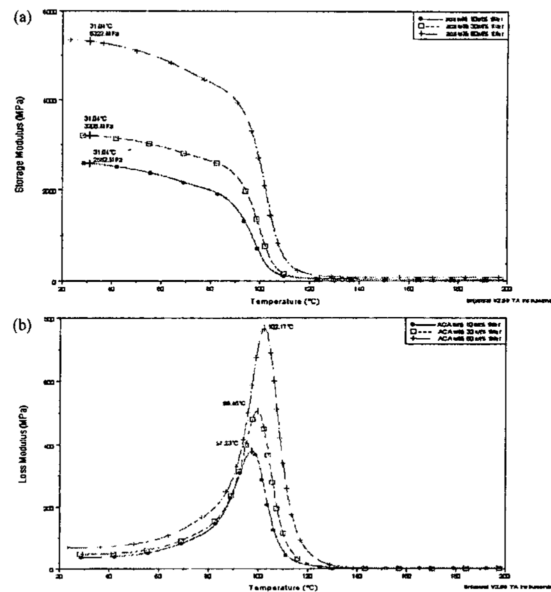

Fig. 4. (a) Storage modulus and (b) loss modulus of ACA samples with 10 wt%, 30 wt%, and 50 wt% fillers.

content increased.[7] Softening of ACA composites is almost the same for three composites at about 120°C. However, the start of the softening process of composites is slightly delayed to a higher temperature when composites contain higher filler contents. And this is presumably due to the high interface area of silica/polymer, when high content of silica fillers are added.[8]

For underfill materials of solder ball flip chip assembly, high modulus is needed to effectively redistribute the solder joints stress to the chip and substrate through the assembly warpage.[9] Similarily, since ACA materials assembled on an organic substrate function as both underfill and electrical conductor, high modulus of ACA by adding high content of fillers is needed.

The optimum modulus of an underfill material for flip chip on an organic substrate generally ranges 6~10 GPa.[10] The content of filler remarkably affects the storage modulus of the cured materials at room temperature. The room temperature storage modulus of the cured ACA materials in this study increases up to 5.3 GPa with 50 wt% filler content. Therefore, high content of filler is preferred, unless the viscosity of ACA composite is too high to be used in the dispensing

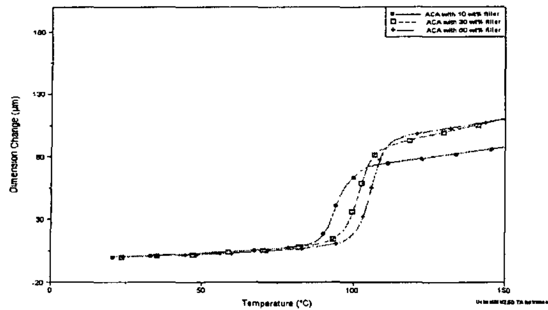

Fig. 5. TMA curves of three ACA composite samples with different content of fillers.

Table 2. Tg^{TMA} and CTE of ACA composites below and above Tg^{TMA}

ACA composite	Tg^{TMA} (°C)	α_1 (ppm/°C)	α_2 (ppm/°C)
ACA with 10 wt% filler	87.62	87.9	3960
ACA with 30 wt% filler	93.53	76.1	3630
ACA with 50 wt% filler	98.77	60.7	3920

process.

3-1-3. TMA results

Fig. 5 show the TMA curves of three ACA composite materials with different filler content. The inflection point of thermal expansion curve is defined as TMA Tg (Tg^{TMA}). This figure shows that higher filler content cause the increase in Tg^{TMA} of the cured samples due to stiffening effect of composite materials with the higher interface area between fillers and epoxy resin as discussed in DMA results. The CTE of the ACA composite below the Tg^{TMA}, defined as α_1, and the CTE above the Tg^{TMA}, defined as α, are important parameters in determining the reliability of the ACA flip chip assembly.

Table 2 indicates that the filler content has significant effect on the α_1, but no noticeable effect on the α_2. From the Tg^{TMA} and the CTE behaviors, higher content of filler is desirable for the reliability improvement of ACA flip chip assembly.

3-1-4. TGA result

The thermogravitational analysis was performed to evaluate the decomposition temperature of ACA composites with different content of fillers. The decomposition temperatures of three ACA composites were almost that same at 393°C due to same epoxy resin used. The filler content in ACA composite doesnt influence on the decomposition temperature, but influence on the weight loss. Fig. 6 indicates weight loss increases as the filler content decreases.

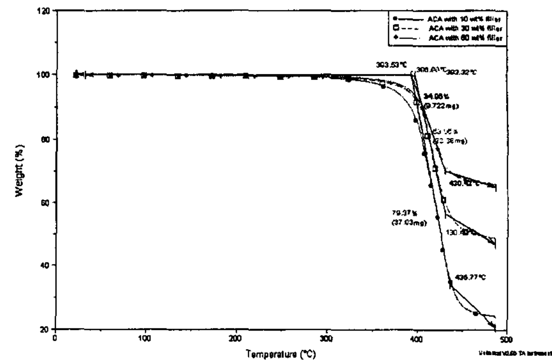

Fig. 6. TGA curves of three ACA samples with different content fillers.

Furthermore these decomposition temperature was also similar to those of commercial underfill materials. The decomposition temperature is one of important properties for reworkable underfill used in flip chip package.[11]

3-2. Reliability Results

The contact resistance variations of flip chip assembly using three different ACA composites during 85°C/85 relative humidity condition for 1000 hrs and 8 °C/dry condition for 1000 hours were shown in the Fig. 7(a) and (b). As can be seen from the Fig. 7(a), the contact resistance of ACA with 30 wt.% and 50 wt.% filler content show very stable value. However, the resistance of ACA with 10 wt.% filler content was stable up to 800 hours and increased a little after 800 hours. No catastrophic failure was observed. The contact resistance of ACA flip chip assembly was stable during 8°C /dry condition regardless of filler content as shown in Fig. 7(b). In summary, the electrical resistance changes were in an acceptable range of below 10% during 85°C/85 relative humidity condition and almost negligible at the dry condition.

The comparison of reliability results between the 85°C/85 relative humidity condition and the 85°C/dry condition reveal that the increase of contact resistance of ACA flip chip assembly is mainly due to the humidity attack on the adhesive layer.[12] This effect of

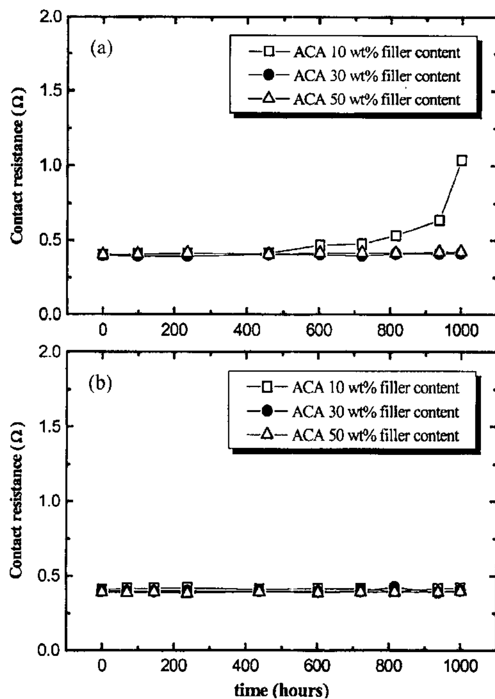

Fig. 7. Contact resistance of flip chip interconnects using ACA with different filler content during (a) 85°C/85%RH test and (b) 85°C/dry condition test.

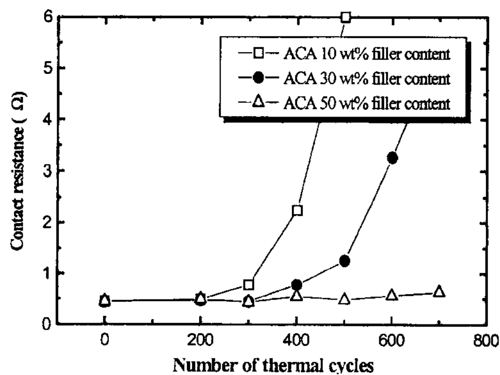

Fig. 8. Contact resistance of flip chip interconnects using ACA with different filler content during thermal cycling test from 60°C to 150°C for 700 cycles.

humidity on the contact resistance of ACA joint was predominant in case of low content of fillers presumably because of higher CTE and lower modulus resulting from higher portion of epoxy resin.

Fig. 8 shows that the contact resistance behaviors of ACA flip chip during −60°C to 150°C thermal cycling condition. The flip chip assembly using ACA with 10 wt.% filler content could not pass 400 cycles, and the assembly using ACA with 30 wt% filler content could not pass 500 cycles. However, flip chip assembly using ACA with 50 wt% filler content ACA 1000 cycles. These results of the thermal cycling test indicates that the filler content in the ACA composite has noticeable effect on the reliability of ACA flip chip assembly on an organic substrate. The higher content of filler in ACAs causes lower CTE and higher storage modulus resulting in a higher reliability of ACA flip chip assembly on an organic substrate during 85°C/85%RH test and thermal cycling test.

Fig. 9 shows the cross-section of flip chip interconnection between chip and organic substrate via ACA with non-conducting particles. Electrical conduction is formed mainly by conductive nickel particles penetrated into the soft Au stud bump surface, not by non-conducting particles. Additionally, the fillet structure formed between peripheral of chip and substrate is very similar to that of conventional solder flip chip with underfill.

4. Conclusion

In this paper, we investigated the effect of non-conducting silica filler content of the ACA composite materials on the curing properties, thermo-mechanical properties, and reliability for the ACA flip chip assembly on an organic substrate. The content of non-conducting filler is the key factor which controls basic properties of ACA composite materials such as curing profile, Tg, CTE, and modulus, and eventually the reliability of ACA flip chip assembly. As the content of non-conducting filler increases, Tg, storage modulus, curing onset and peak temperature increase. And at the same time, the CTE below the Tg decreases. However, assembly using ACA, the content of non-conducting filler addition does not noticeably affect the CTE above the Tg and thermal stability. These effects of non-conducting filler addition on the ACA materials properties were verified by reliability tests. The reliability of ACA flip chip assembly using ACA with higher content of non-conducting filler is significantly better than that of flip chip assembly using conventional ACA or ACA with low content of filler due to lower

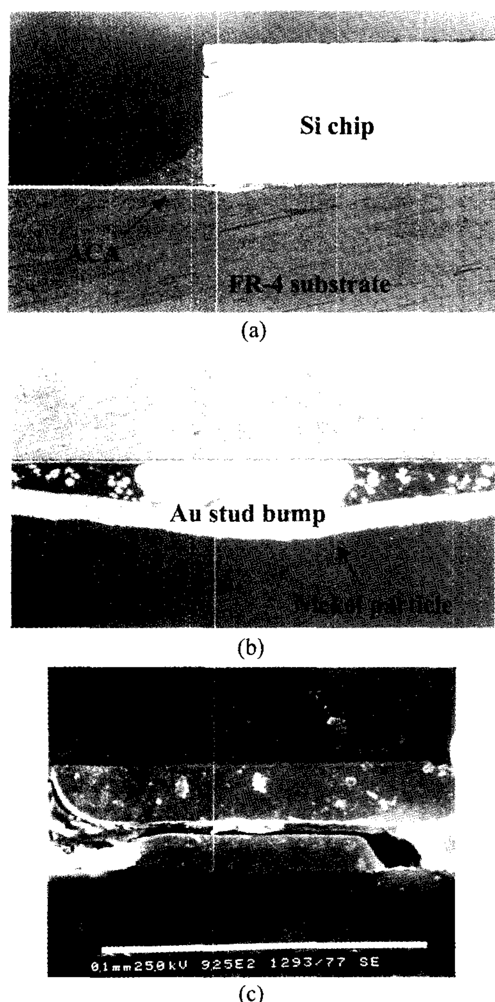

Fig. 9. (a) Optical view of cross section of flip chip (b) enlarged view of interconnection formed by Au stud bump and nickel particles between chip I/O and substrate pad, and (c) SEM cross-section of the ACF flip chip interconnection with Ni/Au bump.

CTE and higher modulus.

Conclusively, the incorporation of non-conductive fillers in the ACA composite material significantly improves the material property of ACAs resulting in better reliability of ACA flip chip assembly on an organic substrate.

5. Acknowledgement

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