

이방성 전도 접착제 물성과 유기 기판 플립 칩의 신뢰성에 미치는 비전도성 충전재의 영향

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Effect of Non-Conducting Filler Additions on Anisotropic Conductive Adhesives (ACAs) Properties and the Reliability of ACAs Flip Chip on Organic Substrates

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초 록 비전도성 충전재를 포함한 개선된 이방성 전도 접착제의 열적/기계적 특성과 이를 이용한 유기 기판용 플립 칩의 신뢰성에 미치는 충전재 양의 영향을 고찰하였다. 비전도성 충전재 양이 다른 개선된 이방성 전도 접착제의 특성을 살펴보기 위해 differential scanning calorimeter (DSC), thermo-gravimetric analyzer (TGA), dynamic mechanical analyzer (DMA), thermo-mechanical analyzer (TMA)을 사용하였다. 비전도성 충전재의 양이 증가함에 따라 열팽창계수는 감소하였고, 상온에서의 storage modulus는 증가하였다. 추가로, 충전재의 양이 증가하면 DSC에 의한 유리전이온도와 TMA에 의한 유리전이온도도 증가하였다. 그러나 TGA 거동은 거의 변화가 없었다.

이방성 전도 접착제를 사용한 유기 기판 플립 칩의 신뢰성 테스트를 위해 열주기 시험, 고온고습 시험, 고온건조 시험을 수행하였는데, 주로 열주기 시험에서 이방성 전도 접착제의 열팽창계수의 영향이 컸다. 비전도성 충전재를 포함해서 낮은 열팽창계수와 높은 storage modulus를 갖는 이방성 전도 접착제에 의해 부착된 플립 칩의 신뢰성이 비전도성 충전재를 포함하지 않은 이방성 전도 접착제에 의한 플립 칩의 신뢰성보다 더 좋게 나타났다.

Abstract We investigated the effect of filler content on the thermo-mechanical properties of modified ACA composite materials by incorporation of non-conducting fillers 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, differential 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 T_g^{DSC} and T_g^{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.

Key words : Anisotropic Conductive Adhesives, flip chip, CTE mismatch, non-conducting filler

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 flip chip assembly using ACAs 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 μ m 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 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. EXPERIMENT

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 with diameter of ave. 2micron of different content (5-45wt.%) and nickel fillers with diameter of ave. 5micron were mixed with liquid epoxy to produce ACAs of 10wt.%, 30wt.% and 50wt.% 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 (bisphenol F type), and a hardener (imidazole type). 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 30min and cutting with 0.6mm thick dimension for the thermo-mechanical characterization such as dynamic mechanical analyzer (DMA), thermo-gravimetric analyzer (TGA) and thermo-mechanical analyzer (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 (T_g) of ACA materials with different filler contents using modulated DSC instrument (by TA Instruments, Model 2920). Aluminum pans containing 7~8mg 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 T_g of the cured ACA samples.

2-2-2. Dynamic Mechanical Analyzer (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 (37.5mm 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 5min. After that, the sample was removed from the oven, cooled down to room temperature, and cut into square with dimensions of about 2 \times 11 \times 35mm. 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 Analyzer (TMA)

The CTE measurement of cured ACA composite sam-

ples 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 5×5×2mm. 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. Thermo-Gravimetric Analyzer (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 N₂ purging (77ml/min in vertical direction and 12ml/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. 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. Figure 1 shows coined stud bumps formed on aluminum

I/Os of test chip.

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



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

Table 1. Specification of test chip and organic substrate.

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

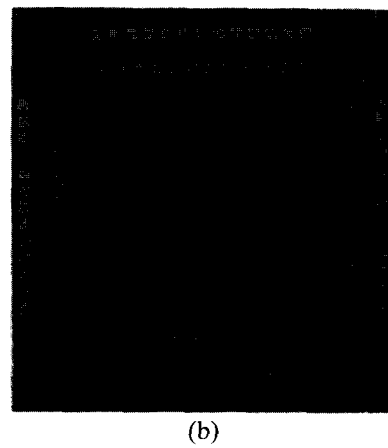
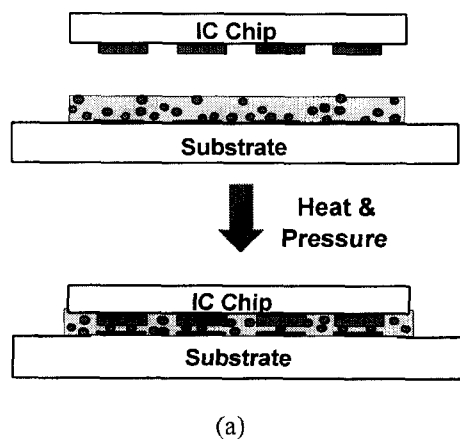


Fig. 2. (a) Schematic of flip chip bonding process using ACA and (b) the appearance of flip chip assembly on an organic substrate such as FR-4 using an ACA composite material.

adhesive pastes without solvent. The substrate used for flip chip assembly was 1mm-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 2~3kgf/cm² and temperature of 150 °C for 5min 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 the schematics of flip chip bonding process using ACA and the appearance of chip on an organic FR-4 substrate 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 resistances 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 -50 °C to 165 °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. Curing behaviors such as curing profile and glass transition temperature between three different ACA composite materials were similar. 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 sharpened the shape of the DSC curves and increased the T_g. The increase of T_g by addition of fillers has been known as general phenomenon.⁷⁾

3-1-2. DMA results

The dynamic mechanical properties of ACA composites from room temperature to 200 °C were studied using DMA. The Fig. 4 shows the variation of the stor-

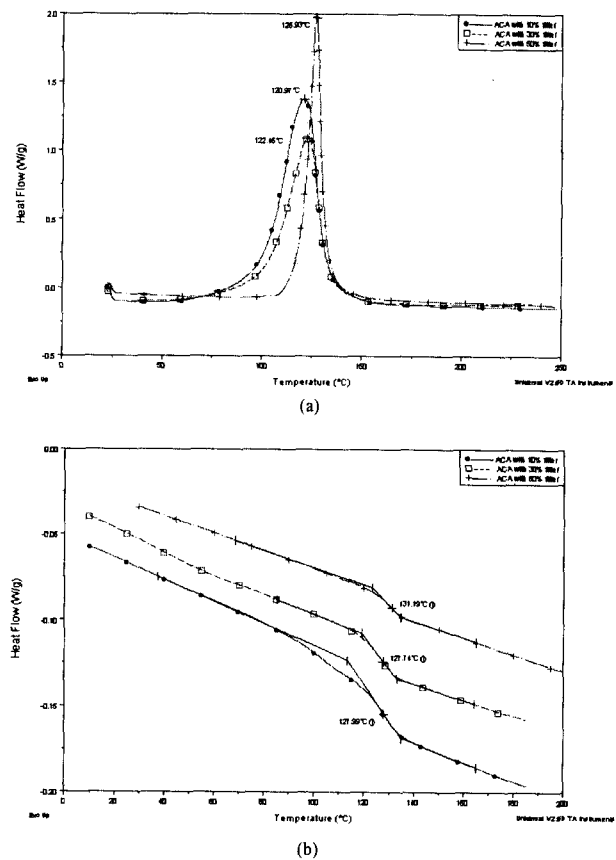
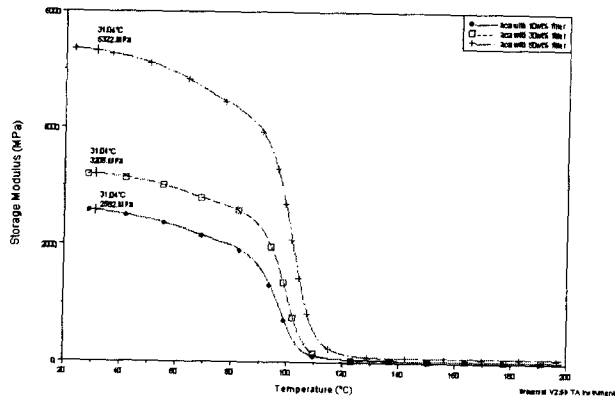


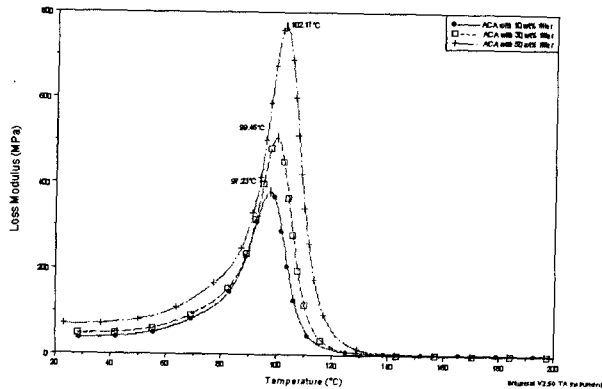
Fig. 3. DSC curves of ACA samples with nickel and silica fillers of different contents (10, 30, 50wt.%) Effect of the filler contents on (a) the curing profiles and (b) the glass transition curves of three ACA composites.

age (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 temperature 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 behaviors can be due to the increased interface area of polymer/filler in ACA composites. Softening points of ACA composites are 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 also 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⁾ Similarly, since ACA materials assembled on an organic substrate function



(a)



(b)

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

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 6~10GPa.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 5.3GPa with 50wt% filler content. Therefore, high content of filler is preferred, unless the viscosity of ACA composite is too high to be used in the dispensing 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 $\alpha 1$, and the CTE above the Tg^{TMA} , defined as $\alpha 2$, are important parameters in de-

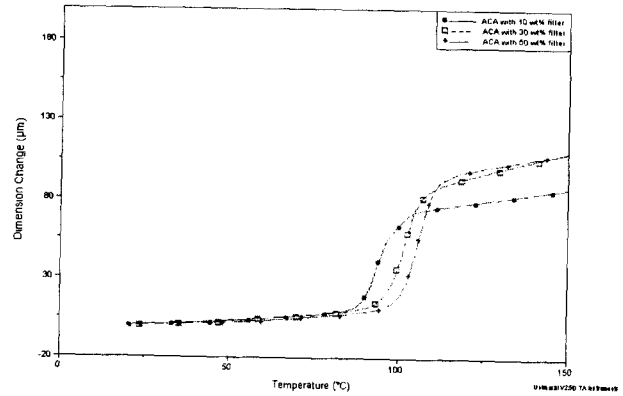


Fig. 5. TMA curves of three ACA composite samples with different content of fillers.

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

ACA composite	Tg^{TMA} (°C)	$\alpha 1$ (ppm/°C)	$\alpha 2$ (ppm/°C)
ACA with 10wt% filler	87.62	87.9	3960
ACA with 30wt% filler	93.53	76.1	3630
ACA with 50wt% filler	98.77	60.7	3920

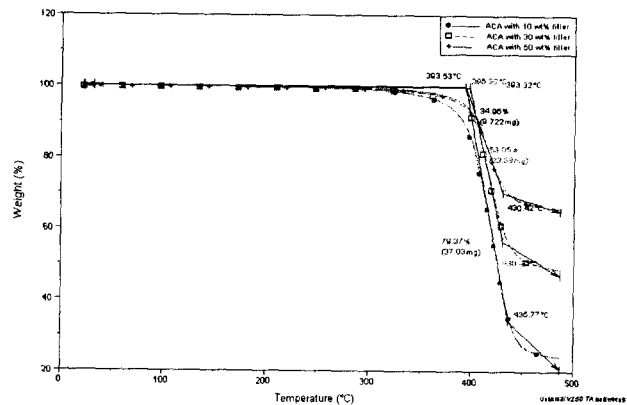


Fig. 6. TGA curves of three ACA samples with different content fillers.

termining the reliability of the ACA flip chip assembly.

Table 2 indicates that the filler content has significant effect on the $\alpha 1$, but no noticeable effect on the $\alpha 2$. 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 thermogravimetric 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 doesn't influence on the decomposition temperature, but influence on the weight loss. Fig. 6 indicates weight loss increases as the filler content decreases.

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.¹⁰⁾

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 85°C/dry condition for 1000 hours were shown in the Fig. 7 (a) and 7(b). As can be seen from the Fig. 7(a), the contact resistance of ACA with 30wt.% and 50wt.% filler content show very stable value. However, the resistance of ACA with 10wt.% 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 85°C/dry condition regardless of filler content as shown in Fig. 7(b). In summary, the electrical

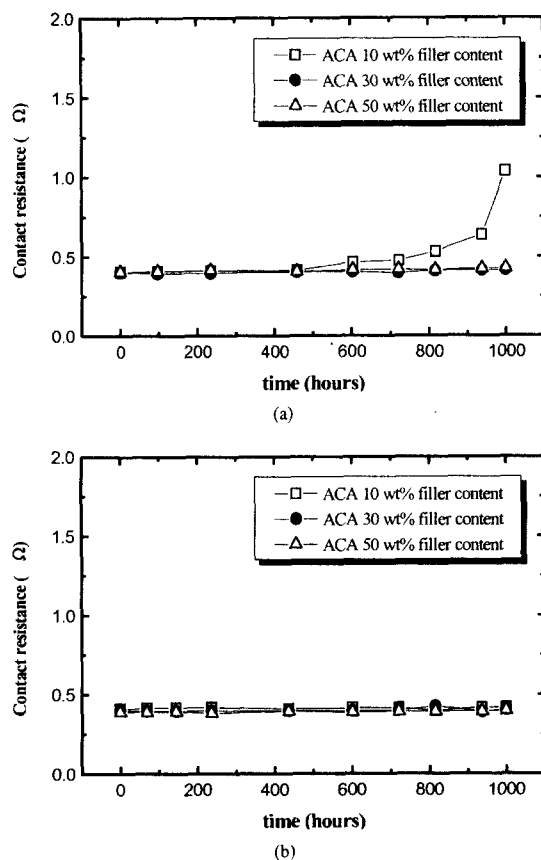


Fig. 7. Contact resistance of flip chip interconnects using ACA with different filler content during (a) 85°C/85%RH test and (b) 85°C/dry condition test.

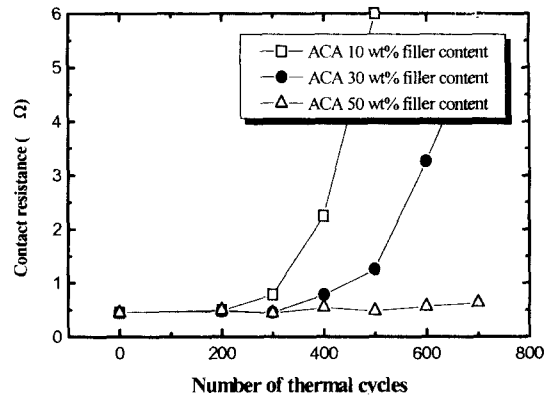


Fig. 8. Contact resistance of flip chip interconnects using ACA with different filler content during thermal cycling test from -50°C to 165°C for 700 cycles.

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.¹¹⁾ This effect of humidity on the contact resistance of ACA joint was predominant in case of low content of fillers presumably because of higher CTE, lower modulus, and higher water absorption resulting from higher portion of epoxy resin.

Fig. 8 shows that the contact resistance behaviors of ACA flip chip during -50°C to 165°C thermal cycling condition. The flip chip assembly using 10wt.% filler content ACA could not pass 400 cycles, and the assembly using 30 wt.% filler content ACA could not pass 500 cycles. However, flip chip assembly using 50 wt.% filler content ACA passed 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.

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, T_g,

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, 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 higher content of non-conducting filler is significantly better than that of non non-conducting filler added ACAs due to lower 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 ACA flip chip assembly on an organic substrate reliability.

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