Novel Nonconductive Adhesives/Films with Carbon Nanotubes for High Performance Interconnects

Hongjin Jiang[1], Myung Jin Yim[2], Kyoung-sik Moon[1] and C. P. Wong[1]
[1] School of Materials Science and Engineering and Packaging Research Center,
Georgia Institute of Technology, Atlanta, GA. 30332-0245
Phone: 404-894-8391, Fax: 404-894-9140, Email: cp.wong@mse.gatech.edu
[2] Intel Corporation, Flash Memory Group
5000 W. Chandler Blvd, Chandler, AZ 85226

Abstract

Novel nonconductive adhesives/films (NCAs/NCFs) with carbon nanotubes (CNTs) for high performance interconnects were developed. A small amount of CNTs (0.03 wt%) was dispersed into the NCAs/NCFs to increase the thermal conductivities and at the same time to decrease the coefficient of thermal expansion (CTE) for high thermo-mechanical reliability of the NCAs/NCFs interconnect joints. The thermal mechanical analyzer measurements showed that the CTE value of the 0.03 wt % CNTs filled NCAs/NCFs was significantly decreased. Current-voltage characterizations showed that the current carrying capabilities of the CNTs (0.03 wt%) filled NCAs/NCFs were increased 14% comparing to the unfilled NCAs/NCFs due to the more efficient thermal dissipation.

Introduction

Lead, a major component in solder, has long been recognized as a health threat to human beings. Polymer-based conductive adhesives are proposed as one of the lead-free candidates, such as isotropic conductive adhesives (ICAs) [1], anisotropic conductive adhesives/films (ACAs/ACFs) [2] and nonconductive adhesives/films (NCAs/NCFs) [3]. The ICAs generally consist of an epoxy resin with high loading of conductive fillers and conduct electricity equally in all directions (Figure 1 (a)). The ACAs/ACFs have lower conductive filler content and thus provide unidirectional conductivity in the vertical or Z direction (Figure 1 (b)). The NCAs/NCFs, on the other hand, do not consist of any conductive fillers, which maintain pure mechanical contacts between the bumps and pads by the compressive force (Figure 1 (c)).

Among all the conductive adhesives, NCAs/NCFs are considered most popular for flip-chip assemblies due to their low cost. Conductive joints with NCAs/NCFs provide a number of advantages compared to other adhesive bonding techniques. The size reduction of electronic devices can be realized by the shrinkage of the package and the chip. Further advantages include ease of processing, good compatibility with a wide range of contact materials, low temperature cure and so on.

In spite of the advantages of NCAs/NCFs joints, there are still some challenging properties of NCAs/NCFs. The thermo-mechanical reliability of the NCAs/NCFs joints is poor due to high thermal stress caused by the coefficient of thermal expansion (CTE) mismatch between the epoxy materials, devices and substrates. At the same time, the thermal conductivities of the NCAs/NCFs materials are poor too, because of the absences of conductive fillers. The heat generated at NCA/NCF joints under high current density can not be dissipated out efficiently. Therefore, the implementations of NCAs/NCFs as interconnect materials for high performance device applications, such as microprocessor and application specific integrated circuit (ASIC) are limited.

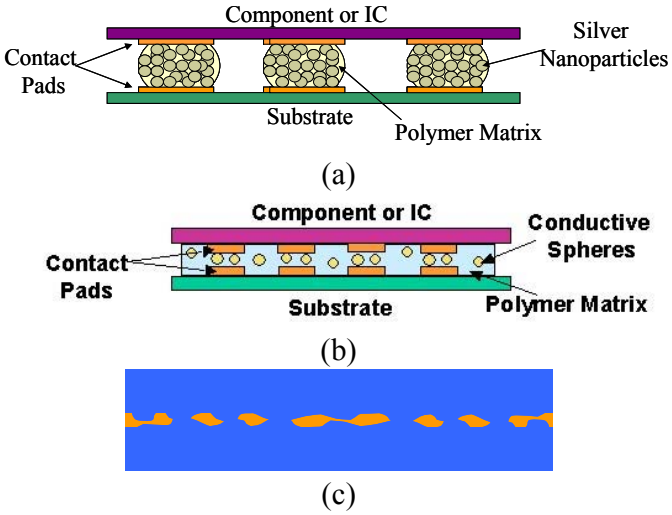


Figure 1. Schematic illustration of (a) ICA, (b) ACA/ACF and (c) NCA/NCF joints

In this study, a novel NCAs/NCFs with the carbon nanotubes (CNTs) for high performance interconnects was developed. CNTs offer many promising characteristics for future electronic and device applications due to their extremely high thermal conductivities [4], outstanding mechanical properties [5], very high electrical conductivities by the ballistic electron transport effect [6] and a lower CTE value (negative at room temperature) [7]. A small amount of CNTs (0.03 wt%) was dispersed into the NCAs/NCFs to increase the thermal conductivities and at the same time to decrease the CTE of the NCAs/NCFs joints without degrading the electrically anisotropic conductivity of NCAs/NCFs joints. The high thermal conductivity of NCAs/NCFs will enable a higher current carrying capability and the lower CTE will enhance the thermo-mechanical reliability of the device. The thermal mechanical analyzer was used to study the CTE values of the CNTs filled NCAs/NCFs. The electrical properties and current carrying capabilities were studied for both the CNTs filled NCAs/NCFs and

unfilled NCAs/NCFs. The other material properties of NCAs/NCFs joints, such as the curing profile and thermal stability were reported as well.

Experimental

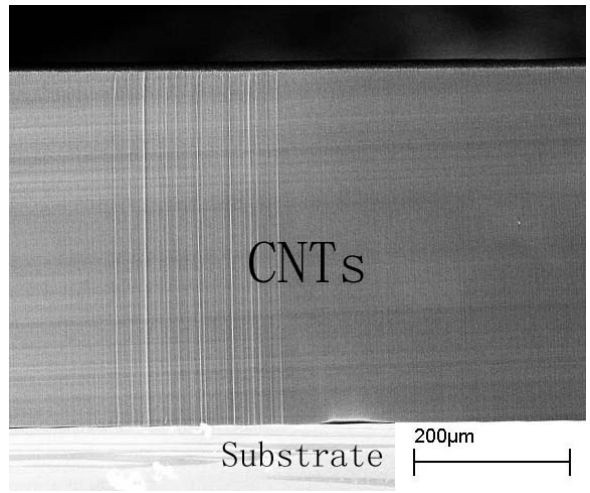
NCAs/NCFs materials

The CNTs were synthesized by the chemical vapor deposition (CVD) method. The detailed experimental procedures used to fabricate CNTs were described in our previous paper [8]. A small amounts of CNTs (0.03 wt%) were dispersed into the epoxy resin by a blender. After the uniform dispersion of CNTs in the epoxy resin, the curing agent (30 wt%) was added. The mixture was then stirred again for 1 hour to achieve the well dispersed NCAs/NCFs. Finally, the mixtures were degassed under a vacuum for 3 hours to eliminate the entrapped air.

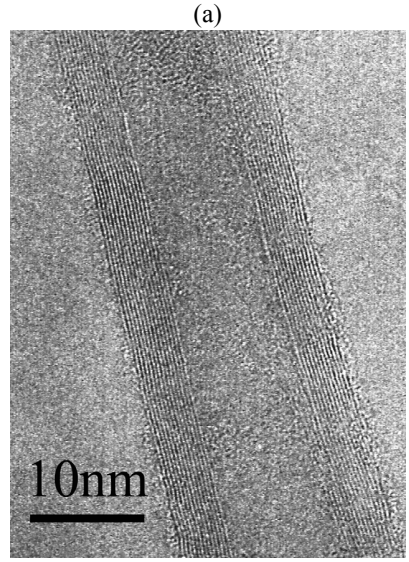
Characterization

Scanning electron microscopy (SEM) was used to characterize the morphologies of the as-synthesized CNT films. The SEM is a JEOL 1530 equipped with a thermally assisted filed emission gun operating at 10 KeV. High resolution transmission electron microscopy (HRTEM, Hitachi 2000K TEM) were used to study the morphology of CNTs. TEM specimens were prepared by dispersing a few drops of the CNT solutions onto a carbon film supported by copper grids. A thermogravimetric analyzer (TGA, 2050 from T A Instruments) was used to investigate the thermal stability of NCAs/NCFs joints. The curing behavior of the NCAs/NCFs was studied by a differential scanning calorimeter (DSC, TA Instruments, model 2970). Thermal mechanical analyzer (TMA, TA Instruments, model 2940) was used to study the CTE of the NCAs/NCFs. The electrical resistance and current carrying capability of NCF joints (contact area: 100 × 100 μm^2) on a Au-finished test vehicle was measured by a four-point probe method. The applied currents were varied from 0.5 to 4.2 A by a power supply (HP model 6553A, HP Hewlett Packard, Palo Alto, CA) and the voltage of the interconnect joints were measured by a Keithley 2000 multimeter (Cleveland, OH). The breakdown voltage of the NCAs/NCFs joints was studied by the curve tracer (type 576).

The thermal conductivity of the NCAs/NCFs was measured by LFA which is a sensitive, contact-free laser flash method (LFA 447). In this method, the flash lamp, samples and the infrared detector are vertically aligned. Both the released energy of flash lamp and the length of the heating pulse can be adjusted via the 32-bit MS windows software named as Nanoflash. The furnace (room temperature to 300 ^{o}C) is directly integrated into the sample holder, creating a small thermal mass and therefore fast heating and cooling are possible. The thermocouple is positioned in the sample carrier for accurately measuring temperatures. Liquid nitrogen cooled Sb infrared detector is used to measure the temperature rise after the light pulse. All the data gathered from the measurements taken using the Nanoflash software is loaded into another software called LFA analysis. This software can do the calculation of thermal properties and make plots for all the measured values.



(a)



(b)

Figure 2. The CNTs synthesized by chemical vapor deposition method: (a) SEM image of CNT films; (B) HRTEM image of a CNT

Results and Discussion

Figure 2 (a) showed the SEM image of the as-synthesized aligned CNT films. Due to the high density of the catalyst layer, the CNTs formed a dense film with good alignment due to the strong Van de Waals force among tubes. Figure 2 (b) is the HRTEM image of the CNTs, which showed that the CNTs had multi wall structure and the diameter of each tube was approximately 20 nm.

A small amount of synthesized CNTs (0.03 wt%) were uniformly dispersed into an epoxy resin to form the NCAs/NCFs. The curing behavior the NCAs/NCFs were first studied by a differential scanning calorimeter. The DSC curves in Figure 3 show the effect of filler contents on the curing profiles of NCA composite materials. From the dynamic scan results, similar curing behaviors of different NCA composite materials were observed. This means that such a small amounts of CNTs will not affect the curing behavior of the epoxy resin.

The thermogravitational analysis was performed to evaluate the thermal stability of NCA/NCF materials with

different content of fillers as shown in Figure 4. The decomposition temperatures of two NCA/NCF composites were almost the same at 400 °C due to same epoxy resin used. The small amount of CNTs in the NCA/NCF composites doesn't influence the decomposition temperature.

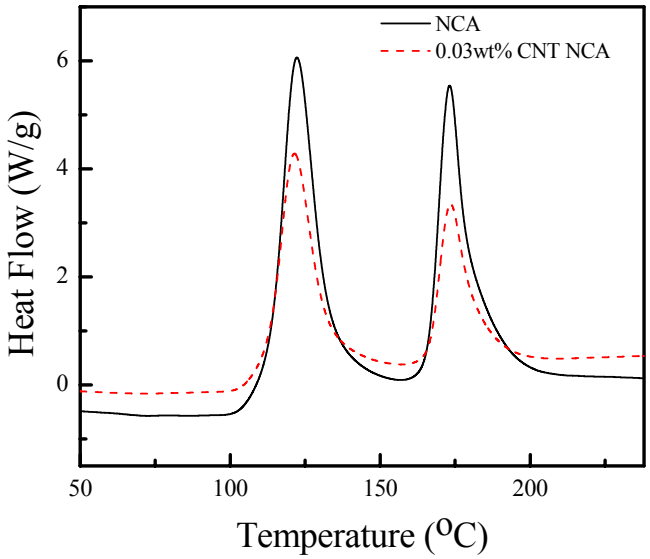


Figure 3. DSC curves of curing profiles of 0.03 wt% CNT filled NCAs/NCFs and pure NCAs/NCFs

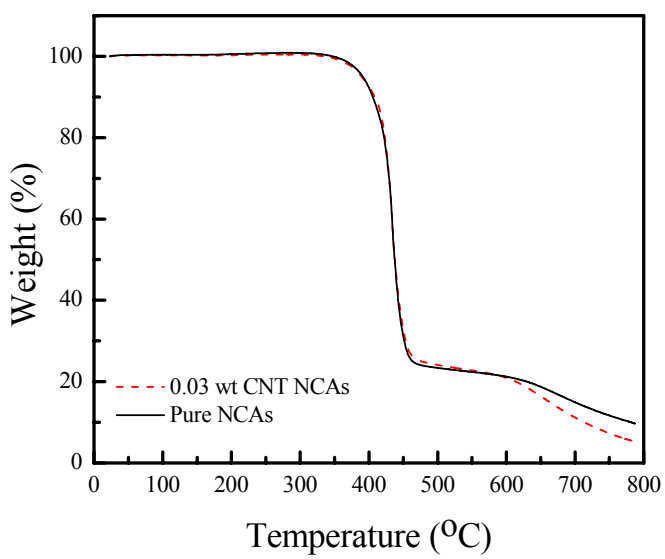


Figure 4. TGA curves of NCAs/NCFs with and without CNTs

CTEs of NCAs/NCFs with/without CNTs were measured using a TMA. A typical TMA curve of the NCAs/NCFs is shown in Figure 5. The inflection point of thermal expansion curve is defined as TMA T_g. α_1 and α_2 are the CTE values of NCAs/NCFs before and after T_g, respectively. Test results are summarized in Table 1. With the increase of the CNT filler loadings, the CTEs of the NCAs/NCFs became smaller due to the lower CTE values of CNT itself [7]. By using 0.03 wt% CNTs, the CTE of the NCAs/NCFs was decreased with a value of 11 ppm/°C. This significant CTE reduction will result in a better thermo-mechanical reliability of the IC device.

Table 1. The CTE values of NCAs/NCFs with different content of fillers

NCAs/NCFs	CTE ppm/°C (α_1)	CTE ppm/°C (α_2)
No CNTs	71.55	197.2
0.02 wt% CNTs	62.3	179.8
0.03 wt% CNTs	60.9	177.8

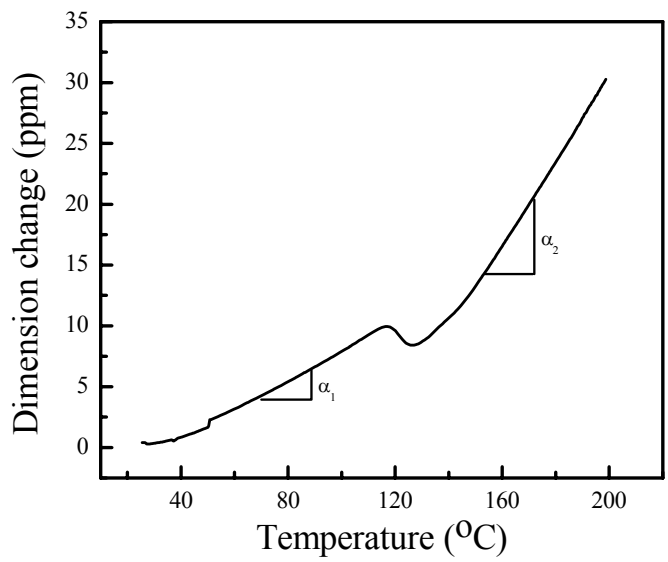


Figure 5. TMA curve of cured NCAs/NCFs materials, showing the definitions of α_1 and α_2.

The electrical performance of the NCAs/NCFs with/without CNTs was studied. The current-voltage (I-V) relationship and correspondingly current-resistance (I-R) relationship of the NCAs/NCFs joints are shown in Figures 6 and 7, respectively. The current carrying capability (maximum current below which the I-V relationship remains linear) of the NCAs/NCFs without CNTs was 3.7 A, while that of the 0.03 wt% CNTs filled NCAs/NCFs was 4.2 A as shown in Figure 6. The contact resistances of NCAs/NCFs joints without and with 0.03 wt% CNTs were around 5.6×10^{-4} and 4.6×10^{-4} ohm, respectively as shown in Figure 7. The current carrying capability of the 0.03 wt% CNTs filled NCAs/NCFs was improved by ~14 % and the contact resistance was decreased by ~ 20%. The significantly improved electrical properties of the 0.03 wt% CNT filled NCAs/NCFs could be attributed to the more efficient dissipation of heat generated by the small amount of CNTs and therefore enable higher current carrying capabilities of the joints

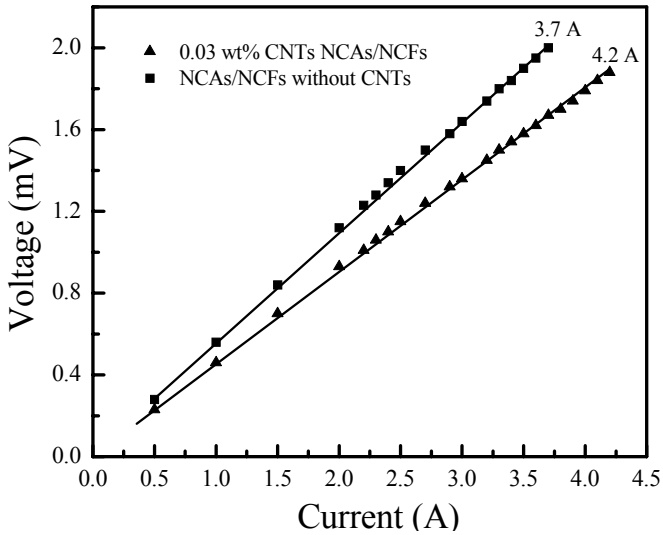


Figure 6. The I-V curves of NCAs/NCFs with and without CNTs

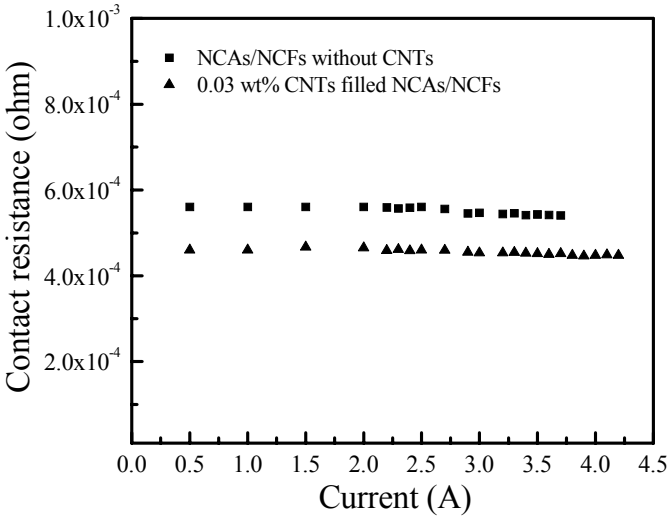


Figure 7. The contact resistance of NCAs/NCFs with/without CNTs

Thermal conductivities of CNT/epoxy composites have been widely studied and the enhancement of thermal conductivity with the increase of filler content was already observed [9-11]. In this paper, LFA was used to study the thermal conductivities of NCAs/NCFs without/with 0.03 wt% CNTs at different temperatures (Figure 8). It was observed that the 0.03 wt% CNTs resulted in an enhancement of the thermal conductivity of the NCAs/NCFs. For instance, at 25 ^{o}C, the thermal conductivity of the 0.03 wt% CNTs filled NCAs/NCFs was around 0.128 W/mK, compared to the unfilled NCAs/NCFs with 0.109 W/mK, an enhancement of 17%. And an enhancement of 11%, 19%, 23% was obtained at 50 ^{o}C, 75 ^{o}C and 100 ^{o}C, respectively. These small amounts of CNTs could help dissipate the heat out more efficiently and therefore enable higher current carrying capabilities of the NCAs/NCFs joints.

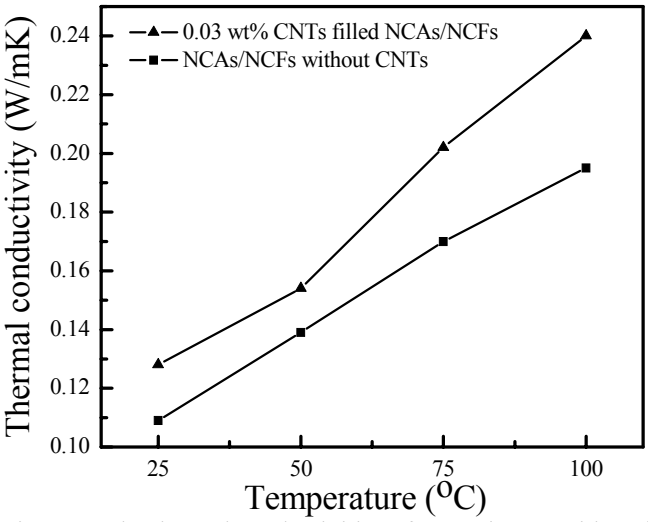


Figure 8. The thermal conductivities of NCAs/NCFs with and without CNTs

The breakdown voltage of the NCAs/NCFs was studied by a curve tracer. The results showed that the breakdown voltage for both the unfilled NCAs/NCFs and 0.03 wt% CNTs filled NCAs/NCFs was larger than 1700 V with a film thickness of around 70 μm. The breakdown voltage characterizations confirmed that the 0.03 wt% CNTs in NCAs/NCFs didn't degrade the electrically anisotropic conductivity of NCAs/NCFs joints

Conclusions

Novel NCAs/NCFs have been successfully prepared for high performance electronic interconnect applications. By using a small amount of CNTs (0.03 wt%), the CTE of the NCAs/NCFs was decreased with a value of 11 ppm/^{o}C and this significant CTE reduction will result in a higher thermo-mechanical reliability of the NCAs/NCFs joints. At the same time, the current carrying capability of the 0.03 wt% CNTs filled NCAs/NCFs was increased by 14% comparing to the unfilled NCAs/NCFs, which is due to the high thermal conductivity of the CNTs and the electronic system heat flux can be dissipated more efficiently.

References

1. Jiang, H., Moon, K., Li, Y., Wong, C. P., "Surface functionalized silver nanoparticles for ultrahigh conductive polymer composites", *Chem. Mater.* Vol. 18, No. 13 (2006), pp. 2969-2973.
2. Li, Y., Moon, K., Wong, C. P., "Enhancement of electrical properties of anisotropically conductive adhesive joints via low temperature sintering", *J. Appl. Polym. Sci.* Vol. 99, No. 4 (2006), pp. 1665-1673.
3. Yim, M. J., Hwang, J. S., Kwon, W., Jang, K. W., Paik, K. W., "Highly reliable non-conductive adhesives for flip chip CSP applications", *IEEE Trans. Elec. Pack. Manufac.* Vol. 26, No. 2 (2003), pp. 150-155.
4. Berber, S., Kwon ,Y. K., Tomanek, D., "Unusually thermal conductivity of Carbon nanotubes", *Phys. Rev. Lett.* Vol. 84, No. 20 (2000), pp. 4613-4616.

5. Ajayan, P. M., "Nanotubes from carbon", *Chem. Rev.* Vol. 99, No. 7 (1999), pp. 1787-1799.
6. Dresselhaus M. S., Dresselhaus G. and Avouris P. *Carbon Nanotubes*; Springer: Berlin, 2001.
7. Yosida, Y., "High-temperature shrinkage of single-walled carbon nanotube bundles up to 1600K", *J. Appl. Phys.* Vol. 87, No. 7 (2000), pp. 3338-3341.
8. Jiang, H., Zhu, L., Moon, K., Wong, C. P., "The preparation of stable metal nanoparticles on carbon nanotubes whose surfaces were modified during production" Carbon Vol. 45, No. 3 (2007), pp. 655-661.
9. Bryning, M. B., Milkie, D. E., Islam, M. F., Kikkawa, J. M., Yodh, A. G., "Thermal conductivity and interfacial resistance in single-wall carbon nanotube epoxy composites", *Appl. Phys. Lett.* Vol. 87, (2005), pp. 161909-1-3.
10. Gojny, F. H., Wichmann, M. G., Fiedler, B., Kinloch, I. A., Bauhofer, W., Windle, A. H., Schutle, K., "Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites", *Polymer* Vol. 47, (2006), pp. 2036-2045.
11. Moisala, A., Li, Q., Kionloch, I. A., Windle, A. H., "Thermal and electrical conductivity of single- and multi-walled carbon nanotube-epoxy composites", *Comp. Sci. Tech.* Vol. 66, (2006), pp. 1285-1288.