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ELECTRICAL AND MECHANICAL CHARACTERIZATION OF MWNT FILLED CONDUCTIVE ADHESIVE FOR ELECTRONICS PACKAGING

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ABSTRACT OF DISSERTATION

Jing Li

The Graduate School

University of Kentucky 2008

ELECTRICAL AND MECHANICAL CHARACTERIZATION OF MWNT FILLED CONDUCTIVE ADHESIVE FOR ELECTRONICS PACKAGING

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

> By Jing Li

Lexington, Kentucky

Director: Dr. Janet K. Lumpp, Professor of Electrical Engineering Lexington, Kentucky

2008

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ABSTRACT OF DISSERTATION

ELECTRICAL AND MECHANICAL CHARACTERIZATION OF MWNT FILLED CONDUCTIVE ADHESIVE FOR ELECTRONICS PACKAGING

Lead-tin solder has been widely used as interconnection material in electronics packaging for a long time. In response to environmental legislation, the lead-tin alloys are being replaced with lead-free alloys and electrically conductive adhesives in consumer electronics. Lead-free solder usually require higher reflow temperatures than the traditional lead-tin alloys, which can cause die crack and board warpage in assembly process, thereby impacting the assembly yields. The high tin content in lead-free solder forms tin whiskers, which has the potential to cause short circuits failure. Conductive adhesives are an alternative to solder reflow processing, however, conductive adhesives require up to 80 wt% metal filler to ensure electrical and thermal conductivity. The high loading content degrades the mechanical properties of the polymer matrix and reduces the reliability and assembly yields when compared to soldered assemblies.

Carbon nanotubes (CNTs) have ultra high aspect ratio as well as many novel properties. The high aspect ratio of CNTs makes them easy to form percolation at low loading and together with other novel properties make it possible to provide electrical and thermal conductivity for the polymer matrix while maintaining or even reinforcing the mechanical properties. Replacing the metal particles with CNTs in conductive adhesive compositions has the potential benefits of being lead free, low process temperature, corrosion resistant, electrically/thermally conductive, high mechanical strength and lightweight. In this paper, multiwall nanotubes (MWNTs) with different dimensions are mixed with epoxy. The relationships among MWNT's dimension, volume resistivity and thermal conductivity of the composite are characterized. Different loadings of CNTs, additives and mixing methods were used to achieve satisfying electrical and mechanical properties and pot life. Different assembly technologies such as pressure dispensing, screen and stencil printing are used to simplify the processing method and raise the assembly yields. Contact resistance, volume resistivity, high frequency performance, thermal conductivity and mechanical properties were measured and compared with metal filled conductive adhesive and traditional solder paste.

KEYWORDS: solder, conductive adhesives, carbon nanotube (CNT), multiwall nanotue (MWNT), epoxy.

Jing Li

02/20/2008

ELECTRICAL AND MECHANICAL CHARACTERIZATION OF MWNT FILLED CONDUCTIVE ADHESIVE FOR ELECTRONICS PACKAGING

By Jing Li

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02/20/2008

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TABLE OF CONTENTS

ACKNO	WLED	GEMENT	iii
TABLE (OF COI	NTENTS	1V
LIST OF	TALB	ED 2ES	Vl
LIST OF	FILES		ix
Chapter1	Intr	oduction	1
Chapter2	Bac	kground	3
2.1	Elect	ronics Packaging Technologies	3
2	2.1.1	IC packaging	3
2	2.1.2	Board Assembly	7
2.2	Lead	free trend in Electronics Packaging	9
2.3	Elect	rically Conductive Adhesive	10
2	2.3.1	Isotropic and Anisotropic Conductive Adhesives	12
2	2.3.2	Percolation and Formation of Conductivity in ICA	14
2.4	Carbo	on Nanotubes	15
2	2.4.1	Structure and properties of Carbon Nanotube	16
2	2.4.2	Synthesis and Purification of Carbon Nanotubes	17
Chapter3	Mo	del of MWNT/epoxy Composite	24
3.1	Elect	rical conductivity of Epoxy/MWNT composite	24
3.2	Mech	anical strength of Epoxy/MWNT composite	26
3.3	Therr	nal conductivity of Epoxy/MWNT composite	28
Chapter4	MW	/NT/EPOXY COMPOSITE PREPARATION	33
4.1	MWI	VI Dispersion and Mixing	
4.2	Curin	ig kinetics of MWNI/epoxy composite	36
4.3	Shatt	er Milled MWNT	37
Chapter5 5.1	Exp Volur	eriments and Results Discussion ne Resistivity Measurement	49 49
5	5.1.1	Relation between MWNT loadings and volume resistivity	50
5	5.1.2	Relation between aspect ratios of MWNT and volume resistivity	53
5	5.1.3	Resistivity for the mixture of long and short MWNTs	54
5.2	Conta	act resistance measurement	55
5.3	Scatte	ering Parameters Measurement	55
5.4	Lap S	Shear Test	56

5.5	Die Shear Test	57
5.6	Thermal Conductivity Measurement	58
5.7	Glass Transition Temperature Measurement	62
5.8	Accelerated aging test	63
Chapter6 REFEREN VITA	Conclusion and Future Work	88 90 93

LIST OF TALBES

MWNT loadings
Table 2: MWNT aspect ratios for volume resistivity samples 65 Table 2: Volume resistivity for different leadings of MWNT with different ement
Table 2: Valume resistivity for different loadings of MWNT with different equat
Table 5. Volume resistivity for different loadings of www.vi with different aspect
ratio 66
Table 4: Volume resistivity of epoxy mixed with different ratios of long and short
MWNT

LIST OF FIGURES

Figure 1: Comparison of wedge bonding and ball bonding	. 19
Figure 2: Structure of TAB polymer tape	. 20
Figure 3: Structure of ILB (a) and OLB (b)	. 21
Figure 4: Bump forms for flip chip: (a) solder bump, (b) plated stub bump, (c) w	vire
stub bump, (d) adhesive bump	. 22
Figure 5: Junction schematic of ACA	. 23
Figure 6: Schematic for the band gap of metal, semiconductor and insulator	. 30
Figure 7: Volume resistivity vs. filler loading	. 31
Figure 8: schematic of resistance model in percolated linkage	. 32
Figure 9: equilibrium contact angle, θ	. 32
Figure 10: SEM image of as-produced MWNT	. 38
Figure 11: SEM images for comparison of dispersion: (a) 0.4 wt% of MW	'nΤ
dispersed in epoxy without ultrasonication, (b) 0.4 wt% of MWNT dispersed	d in
epoxy with ultrasonication.	. 39
Figure 12: Microscopy images for comparison of wetting: (a) cured MWNT/ep	oxy
composite on copper pad, (b) reflowed commercially available 63Sn/3	7Pb
solder on copper pad	. 40
Figure 13: curing profile for 2 wt% loading of MWNT/epoxy composite	. 41
Figure 14: curing profile for 4 wt% loading of MWNT/epoxy composite	. 42
Figure 15: curing profile for 8 wt% loading of MWNT/epoxy composite	. 43
Figure 16: curing profile for neat epoxy	. 44
Figure 17: Broken shatter milled MWN1	. 45
Figure 18: Open-ended shatter milled MWN1	. 46
Figure 19: TEM micrograph of shatter milled MWN1	. 4/
Figure 20: TEM micrograph of shatter milled MWN1	. 48
Figure 21: Method for measuring bulk volume resistivity	. 68
Figure 22: Sample design for volume resistivity measurement	. 69
Figure 23: Log (p) volume resistivity versus MWN1 loading for as-produced r	ngn
Eigure 24: SEM micrograph for ton surface	. 70
Figure 24. SEM micrograph of gross setion	. /1
Figure 25. SEM micrograph for 8 wt% MWNT/apoyy composite after argon pla	. 12
othing for 8 minutes	5111a 72
Figure 27: Contact resistance measurements at 2 4 and 8 wt% loading of	. 75
produced MWCNT in enovy cured with applied weight	а5- 7Л
Figure 28: Schematic of the high frequency test hoard	. 74
Figure 20: Input reflection coefficient (S_{11}) for solder silver filled adhesive	. 75 and
MWCNT filled enovies from 50 MHz to 3 GHz	76
Figure 30: Forward transmission coefficient (s_{21}) for solder silver filled adhesive	and
MWCNT filled enoxies from 50 MHz to 3 GHz	77
Figure 31: Lan shear test sample	78
Figure 32: Comparison of lap shear strength for silver filled ICA and various ra	tios
of as-produced and shatter milled MWNT in epoxy	.79
Figure 33: Schematic of die shear test	. 80
Figure 34: Structure of LFA	. 81
-	

Figure 35: Laser flash thermal diffusivity analysis for as-produced MWNT/ep	poxy
composite and neat epoxy	82
Figure 36: thermal diffusivity analysis for mixed MWNT/epoxy composites and	pure
as-produced MWNT/epoxy composites	83
Figure 37: Measured heat capacity for 8 wt% MWNT/epoxy composite	84
Figure 38: DSC analysis showing Tg for 2 wt% MWNT/epoxy composite	85
Figure 39: DSC analysis showing T _g for 8 wt% MWNT/epoxy composite	86
Figure 40: volume resistivity in accelerated aging test	87

LIST OF FILES

1: JingLi_dissertation.pdf2.3M	ИB
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Chapter1 Introduction

In electronics packaging, chips and components need to be assembled into mechanically robust and electrically functional devices or final products. In different levels of electronic assemblies, solder alloys are widely used to provide both electrical and mechanicall interconnections. Solder be used as bump interconnection in flip chip assembly, die attach material in wirebond assembly or interconnection material for through-hole and surface mount technologies in printed circuit board assembly. Solder is applied as solder paste by screen printing, stencil printing or pressure dispensing, then a reflow oven activates the flux and melts the solder. Molten solder is also used in wave soldering of surface mount and through-hole components. Both wave soldering and solder reflow rely on molten solder wetting on metal surfaces to define shape of the solder joints and to prevent short circuit bridging across insulated spaces between metal features. In manufacturing facilities world wide, the traditional tin-lead solder alloys are being replaced by lead-free materials in response to the international restriction on the use of hazardous substances legislation (RoHS).

Even before RoHS, metal filled isotropic conductive adhesives (ICAs) were commercially available as viable alternatives to soldering for die attach and component assembly. ICA material properties are significantly different than solder and depend on the choice of polymer matrix composition. For example, ICA products may be thermoplastic or thermosetting and may wet both conductor and insulator surfaces. The same dispensing methods used for solder paste are employed to apply an ICA to printed circuit boards with appropriate process control tolerances to prevent bridging. As composite materials, the polymer matrix of an ICA provides adhesion to the circuit board pads and component leads while compressing the conductive particles together to form the electrical path. Traditional metal filled ICAs require high loadings of conductive filler material to overcome the percolation threshold and ensure electrical conductivity. Such a high volume fraction of filler degrades the mechanical properties of the polymer matrices. With conventional metal filled conductive adhesives, only a small portion of the shear strength of polymer matrices can be retained. When the fillers are randomly distributed cylinders, the critical volume fraction for percolation is proportional to the inverse of the aspect ratio and surface area. Low percolation thresholds are expected, therefore, with long narrow filler particles providing large surface areas for particle to particle contact.

High aspect ratio, large surface area multiwall carbon nanotubes (MWNTs) have the potential as ICA filler particles to reach the percolation threshold with small volume fraction loading. The MWNT used in the present study have aspect ratios from 250 to 2500. MWNT are electrically conductive independent of synthesis method and have extremely high strength to weight ratio offering the potential to improve the stiffness of the polymer matrix.

In this research, we are focusing on optimizing the volume resistivity and processability of carbon nanotube filled epoxies. Dispersion, loading and pot life of MWNT into several different resins are addressed to demonstrate their potential application in electronic assemblies. MWNT/epoxy composites with different loadings of MWNT were prepared. Electrical, mechanical and thermal properties were tested. Accelerated aging testing was also carried out. Replacing metal fillers in ICAs with MWNT has the potential benefits of being lead free, corrosion resistant, high mechanical strength and lightweight.

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Chapter2 Background

2.1 Electronics Packaging Technologies

Electronic products usually consist of integrated circuit (IC) packaging to integrate the ICs with other devices into components, and system level packaging to integrate the active ICs and passive components to form a complete system. IC packaging is the first level packaging to provide mechanical and environment protection, heat dissipation and electrical connections for the semiconductor devices. System level packaging is referred to as second level packaging to provide interconnection of all devices on the system level board as well mechanical support and heat dissipation for the system.

In this section, the major electronic packaging and assembly technologies are briefly summarized.

2.1.1 IC packaging

After wafer fabrication and singulation, the bare die or IC devices are electrically connected to a substrate or package so that they can be handled and tested. There are three primary IC to package interconnection technologies: wire bonding, tape automated bonding (TAB), and flip chip bonding.

Wirebonding

Wirebonding is the most widely used technique for its cost effectiveness and flexibility. In this technology, an aluminum or gold wire, typically 1 mil in diameter is attached between each of the I/O pads on the IC chip and the corresponding package pin, one at a time. Depending on the bonding agent (heat and/or ultrasonic energy), the bonding process can be one of the three major processes: thermocompression bonding, ultrasonic bonding, and thermosonic bonding. The major advantage of wirebonding is the

flexibility of this point to point process. To change wiring, only simple modifications to the data-driven machine program are needed and no hard tooling modification is required. There are two major forms of wirebonds in volume production: ball bonding and wedge bonding. Gold is commonly used for ball bonding and aluminum for wedge bonding. Wedge bonds are mostly used in fine pitch bonding due to the fact that wedge bonds deform the wire only 25% ~30% beyond the original diameter while the ball bonds deform the wire 60%~80% beyond the original diameter. [1] Figure 1 illustrates the structure of wirebond interconnection.

Tape Automated Bonding (TAB)

Tape Automated Bonding (TAB) is an interconnection technology between the substrate and the IC, which uses a prefabricated carrier with copper leads attached to the IC pads instead of single wires. This prefabricated carrier is usually made of metallized polymer tape. Copper is a commonly used metal in polymer tapes. It can be electrodeposited on the tape or simply a foil glued to the tape using adhesives. The interconnection patterns are imaged onto the tape by photolithography. TAB technology is based on the fully automated bonding of one end of an etched copper beam lead to an IC and the other end of the lead to a conventional package or PWB. The bonding sites of the IC die, usually in the form of bumps or balls made of gold or solder, are connected to fine conductors on the polymer tape. The polymer tape provides the means of connecting the IC die to the package or directly to PWB. Sometimes the tape on which the IC die is bonded already contains the actual application circuit of the IC. In TAB process, the polymer tape is positioned above the bare die so that the metal tracks on the polymer tape correspond to the bonding sites on the die, as shown in Figure 2. The TAB bonds connecting the die and the tape are known as inner lead bonds (ILB), while those that connect the tape to the package or to external circuits are known as outer lead bonds (OLB). ILB and OLB are separately shown in Figure 3 (a) and (b).

The TAB technology provides several advantages over the wire bonding technology. These advantages include: smaller bonding pad compared to wire bonding

technology, faster area bonding (gang bonding) comparing with individual wire bonding, better electrical performance (noise and frequency) and feasible for know good die test. The disadvantages of TAB technology is the high cost of bonding equipment and designing and fabricating the tape. Therefore TAB has typically been limited to high-volume production applications. The principle use of TAB is as driver connections on LCD panels. [1]

Flip chip

Flip chip is an IC chip interconnection technology in which the IC chips are turned active face down and bonded directly to a printed circuit board or chip carrier substrate. Interconnection between the chip I/O sites and substrate pads is achieved through using bump structures on the chip and bonding material on the substrate to form electrical and mechanical connection. The bump serves several functions in the flip chip assembly: the electrically conductive path from chip to substrate, thermally conductive path to dissipate heat from the chip to the substrate, the mechanical support of the die to the substrate and the short lead to relieve mechanical strain between board and substrate.

The most common bump forms in flip chip devices include solder bump, stub bump and adhesive bump. In solder bumping process, an under bump metallization (UBM) is first made on the chip bond pads by sputtering, plating, or other means. The UBM serves as a compatible layer between the bump and the chip pad metallization. It also defines the solder-wetted area and prevents the corrosion of chip pad metallization. Then solder is deposited over the UBM by evaporation, electroplating, screen/stencil printing, or solder jet printing. Figure 4 (a) illustrates the structure of solder bump.

There are two forms of stub bump: plated stub bump and wire stub bump. Plated stub bumps are formed on the chip I/O pads by electrolytic or electroless plating. The plated stub bump material includes: gold, nickel, copper, gold-tin, nickel-gold and nickelcopper. Attachment of plated stub bumped flip chip is generally by solder or conductive adhesive. The solder paste or conductive adhesive may be applied to the bumps or the substrate bond pads by dipping or stencil printing. Figure 4 (b) illustrates the structure of plated stub bump. Wire stub bumps are formed by using modified ball bonding technique in wirebonding: the wire is fractured after the gold ball is attached on the chip bond pad. The wire stub bumps are most commonly made with 1 mil diameter gold wire. The wire stud bumped flip chips may be attached to the substrate bond pads by conductive adhesives or thermosonic gold-to-gold connection. Figure 4 (c) illustrates the structure of wire stub bump.

The adhesive bumps are made by screen or stencil printing of the conductive adhesive onto the chip pads. The cured adhesive forms adhesive bumps. The attachment of adhesive bumped flip chip is by dipping or printing an additional layer of conductive adhesive on adhesive bumps or the substrate bond pads. Figure 4 (d) illustrates the structure of adhesive bump.

Flip chip processing was originally implemented on ceramic substrates. Alumina ceramic has a coefficient of thermal expansion (CTE) of about 7 ppm/°C, which is close to the silicon CTE. However for organic substrates, flip chips are prone to thermally induced cracking due to the CTE mismatch. The CTE for conventional FR-4 composite circuit board is 16 ppm/°C while the CTE for silicon is about 2.5 ppm/°C. [2] This mismatch can cause cracked solder bumps and even damage the device itself. The global CTE mismatch between chip and substrate board usually causes board warpage. The local CTE mismatch between the adjacent materials at the interfaces of a solder bump usually causes bump crack. This CTE mismatch between chip and substrate can be compensated by applying underfill. Underfill is an adhesive designed to wick into the space between the bottom of the die and the top of the board so that it can bond the die and the board together, compensate the CTE mismatch and protect the bump interconnections from environmental effects. Underfills can be applied by one of the three processing methods: capillary flow, injection flow and compression flow. Besides bonding the bare chip to the substrate, flip chip technology is also related to ball grid array (BGA) assembly and chip scale packaging (CSP). BGAs have been widely used in surface mount technologies and CSPs are growing in popularity.

2.1.2 Board Assembly

After IC packaging processes make individual electrical components ready to be handled, Printed Wiring Board (PWB) assembly processes integrate different electrical components into functional systems. There are two major PWB assembly technologies: through-hole assembly and surface mount assembly. In through assembly, leads of the components are inserted into the conducting plated through holes and soldered on the back side of the PWB. While in surface mount assembly, components can be placed and soldered on both sides of the PWB. Due to the fact that surface mount assembly utilizes both sides of the board and size of surface mount components is usually smaller than comparable through-hole components, surface mount assembly has grown in popularity.

Through-hole assembly

In through-hole assembly, component leads are inserted into the plated holes by hand or by automatic insertion machines. There are three groups of through-hole components: axial, radial and dual-in-line (DIL). The axial components for a board are sequenced onto a ribbon and the ribbon is wounded up on a reel. The axial insertion machine picks the components from the reel, bends the leads and inserts them into the plated through-holes. The insertion machine for radial and DIL components directly picks the component from the reel or stick without sequencing and inserts them into the plated through-holes in board. The through-hole components are soldered on the board by using molten solder in the wave soldering process.

Surface mount assembly

The first step of surface mount assembly is to apply the solder paste onto the pads. Solder paste is a mixture of solder alloy particles, flux and solvent. The application step is realized by pressure dispensing or screen/stencil printing. Pressure dispensing uses air pressure to squeeze the solder paste through the needle of a syringe and deposit the solder paste on the pads one at a time. The dispensing process can be done either manually or by computer controlled programmable dispenser. The amount of solder paste deposited on the pad can be controlled by the combination of air pressure and dispensing time. The pressure dispensing can be used to dispense different materials such as adhesive, solder paste, underfill and flux. However it is usually used in rework or prototype development due to its slow speed. Screen printing offers more flexibility because the screen can be easily photo defined. Stencil print can handle smaller opening sizes, therefore it is more commonly used to print fine patterns. After aligning the pads on the PWB with the openings on the stencil, solder paste is pushed down into the openings by a squeegee and deposited onto the pads. The opening size controls the deposit area and the thickness of the stencil controls the amount of solder paste transferred onto the pads.

After solder paste is deposited on the pads, the components are picked up and placed onto the corresponding pads. This step is usually done by automatic pick and place machines. The PWB is transferred into the pick and place machine and fixed in position. Vision cameras on the machine look for the fiducial marks on the board and automatically calculate the coordinates for each component. Components are picked up from the component feeder by a vacuum nozzle and centered before placed on the PWB to ensure the accurate placement. The centering process can be realized either by mechanical alignment or visual alignment. In mechanical alignment, a mechanical centering device pushes the component to the center position on the nozzle. In the visual alignment, the pick and place machine calculates the difference between the actual component position and the center position on the nozzle and add the difference to the coordinates for placing this component on the PWB.

After components are placed on the PWB, reflowing soldering is needed to provide mechanical bonding as well as electrical and thermal interconnection. Reflow soldering is usually carried out in a reflow oven for surface mount assembly. The reflow profile normally includes four phases: preheat, soak, reflow and cool down. In preheat phase, the temperature is gradually increased to vaporize the solvent in the solder paste. In the soak phase, the flux begins to clean the component leads and the solder pads. In reflow phase, the eutectic solder melts at 183°C and begins to wet the pads and leads. The

peak temperature of reflow phase is normally 215°C to 225°C. The melted solder solidifies in the cool down phase. [1] Wave soldering can also be used when both through-hole components and surface mount components are on the board. In this case, surface components need to be glued onto the board by using nonconductive (insulative) adhesives.

2.2 Lead free trend in Electronics Packaging

Microelectronic assemblies in commercial applications and consumer electronic products are phasing out the use of lead and other hazardous materials in response to the international restriction on the use of hazardous substances legislation (RoHS). RoHS compliant products utilize alternative surface finishes, solder pastes, solder alloys and component lead coatings and require manufacturers to replace or upgrade equipment formerly used to process lead containing materials. For example, tin-copper and tin-silver-copper alloys adequately replace the electrical, thermal and mechanical roles of lead-tin solders but require higher temperatures to melt and reflow. Long term reliability issues such as tin whiskers and silver migration may still plague the performance of the new solder alloys. Even before RoHS legislation set a timeline for the removal of lead from electronics, metal filled polymer adhesives were offered as a viable option to solder. ECAs have been proposed in surface mount technologies as replacement for solder to solve the CTE mismatch problem between the ceramic chip carrier and the glass epoxy substrate board.

Isotropic conductive adhesives (ICA), as an alternative to solder reflow processing, are widely used for die attach and surface mount assemblies. Traditional metal filled ICAs require 25% to 30% volume fraction (up to 80 wt %) to ensure electrical conductivity. Such a high volume fraction degrades the mechanical properties of the polymer matrices. With conventional metal filled conductive adhesives, only a small portion of shear strength of polymer matrix can be retained. According to I. Balberg et al., for randomly distributed cylinders, the critical volume fraction for percolation is

proportional to the inverse of the aspect ratio. [3] Since MWNTs have very high aspect ratio, it is possible to reach the percolation threshold with small volume fraction. As well as MWNTs have extremely high strength to weight ratio, replacing the metal fillers with MWNTs has the potential benefits of being lead free, low process temperature, corrosion resistant, high electrical conductivity, high mechanical strength and lightweight. In recent years, electrical and mechanical properties have been investigated for the MWNT/polymer composites. J.K.W. Sandler et al. reported the percolation threshold for MWNT/polyamide/ABS composite lies between 2 wt% to 3 wt% and 27% increase in Young's modulus for MWNT/polyamide/ABS composite with 7 wt% loading of MWNT. [5]

While consumer electronics represent a large potential market for nanotube filled conductive adhesives, the benefits are also applicable to military and aerospace applications. Weight limitations and reliability in harsh environments are two priorities where the non-metallic conductor may provide improved performance over soldered assemblies. The potential weight savings of MWNT ICA over solder is 83% for the same volume. By eliminating tin and silver from the contact area, MWNT ICA bonded components should exhibit no degradation by silver migration and tin whisker formation. Other metallic corrosion and fatigue mechanisms are also reduced by using polymer adhesives to separate component metal leads from the metal interconnect on the circuit board. Thermal conductivity and mechanical properties need to be evaluated at higher loadings to determine the usefulness of MWNT filled adhesives for thermal management and structural elements.

2.3 Electrically Conductive Adhesive

An electrically conductive adhesive (ECA) is an organic polymer loaded with conductive particles. Polymer-based adhesives are widely used in the electronics industry. However due to their excellent dielectric properties, they are used extensively as electrical insulators. Although a small class of intrinsically conductive polymers (ICPs) does exist, their instability in air, brittleness and difficulty to apply limit them for use as electrically conductive adhesives. In most of current ECA products, conductive filler particles are mixed into the polymer adhesive to provide electrical continuity. Even before RoHS, metal filled isotropic conductive adhesives were commercially available as viable alternatives to soldering for die attach and component assembly. Based on curing properties, ECAs can be classified as thermal curing or UV curing. Based on physical properties after cure, ECAs can be classified as thermoplastic or thermosetting. Based on the direction of electrical conductivity, there are two types of ECAs: isotropic conductive adhesive (ICA) and anisotropic conductive adhesive (ACA).

Both ICA and ACA can be either thermosetting or thermoplastic. Thermoplastic adhesives are all one-part adhesives with the ability to melt after curing when exposed to heat. Thermoplastic adhesives are based on a polymer dispersed in a solvent mixed with conductive filler particles. In the curing process, the solvent is evaporated by heat without chemical reaction. Examples of polymers used are polyamides (nylon), polythenes, PVC and polyimidosilozane. Examples of solvents are butylcellosolvacetate, N-methyl-2-pyrrolidone. Thermoplastic adhesives have virtually unlimited shelf life at room temperature. Due to the elastifying effect in heat, thermoplastic adhesives can reduce the thermal stress in the joint and are reworkable. [6] A disadvantage is a relatively longer curing time compared with most thermosetting adhesives. [7]

Thermosetting adhesives consist of a polymer resin (epoxy, polyamide or silicone are the most frequently used), curing agent, additives and the conductive filler particles. Chemical reaction occurs in curing the thermosetting adhesives. In this reaction, the molecules in the resin and the molecules in the curing agent (or sometimes only in the resin) are bonded together forming a three dimensional polymeric network. In chemistry terms, "thermosetting" is only used for adhesives that involve a chemical reaction at elevated temperatures in curing. When referring to the electrically conductive adhesives, the phrase is used for all adhesives that involve a chemical reaction in curing, including the adhesives whose curing take place at room temperature. Cured thermosetting adhesives do not melt under heating. When the temperature exceeds the glass transition temperature (Tg), the material becomes rubbery and leathery and has great flexibility and toughness. Below Tg the material is hard and often also brittle. There are two subgroups of thermosetting adhesives: one-part and two-part thermosetting adhesives. In one-part thermosetting adhesives, the curing agent is either incorporated in the mixture in an inactive state or "delivered" from the environment. The curing is initiated for example by heat, by humidity from the air, by use of UV-light or by visible light. It is possible to get adhesives that cure at room temperature as well as at higher temperature. Pot life is often a little longer than for one-component adhesives, while shelf life is reduced. In two-part thermosetting adhesives, the resin and the curing agent are delivered separately. The two parts are mixed just before use and the curing reaction is initiated (normally accelerated by heating). Also in this group of adhesives, some of them can be cured at room temperature. One of the disadvantages of the two-part thermosetting adhesives is that the handling of the chemicals is complicated by obtaining the proper ratio of the two components in the mixture and thorough mixing. Also their pot life is comparably short, while shelf life of separate components is long.

2.3.1 Isotropic and Anisotropic Conductive Adhesives

Isotropic conductive adhesive

Isotropic conductive adhesives generally consist of a polymer matrix such as epoxy and conductive filler particles such as silver flakes or spheres. Most of ICAs are epoxy-based thermosetting adhesives and cured by heat. Epoxy resin is considered one of the best adhesives due to its good adhesion to metal, low cost and relative safety of use. The filler particles vary in shape and size as well as in material composition. The most frequently used material for conductive fillers are silver, gold, copper and nickel. Silver has high electrical conductivity and the silver oxide layer, unlike many other metal oxide layers, has good electrical conductivity too. Due to this special characteristic, the ageing of the silver fillers will not result in significantly reduced conductivity in a composition including silver fillers. The disadvantages of silver are its tendency to migrate and the relatively expensive price. Silver is found to be the most frequently used filler particle material in electrically conductive adhesives for surface mount technology. Gold has lower conductivity than silver and is much more expensive, but it has a very low ability to migrate and the oxide layer of gold is also conductive. Thus gold is often chosen for use in military and space electronics to avoid the risk of silver migration. Copper has good conductivity and is not very expensive but in the presence of oxygen it will form a continually growing insulating oxide layer, which reduces the electrical conductivity when exposed to oxygen. Nickel has relatively low electrical conductivity. Work with nickel can cause allergies and nickel dust is found to be carcinogenic. Both copper and nickel are limited to the low cost applications. In addition to the pure metals, composites such as copper and glass plated with silver or gold are also developed as filler material.

The conductive fillers in the ICA composite make contact with each other and form a conductive path to provide electrical conductivity. The volume fraction loading of conductive filler particles in ICA must be higher than the percolation threshold to ensure the electrical conductivity. In the ICA joint, the polymer resin mechanically bonds the component to the substrate and the conductive filler provides electrical conductivity. On one hand the higher loading is desired for better conductivity, on the other the high loading of conductive fillers degrades the mechanical strength of the polymer resin. Therefore there is a tradeoff between the electrical conductivity and mechanical strength in ICA compositions. The volume fraction loading of conductive filler is silver, the corresponding weight percent loading is about 25% to 30%. [8] If the filler is silver, the corresponding weight percent loading is about 78% to 82%. ICAs conduct electricity in all directions and are most widely used in industry to attach passive devices or semiconductor components to the substrate.

Anisotropic conductive adhesive

Anisotropic conductive adhesives are pastes or films of thermoplastics or b-stage epoxies filled with metal particles or metal-coated polymer spheres at much lower levels (0.5% to 5% by volume) than ICAs. The volume fraction of filler in ACAs is far below the percolation threshold, thus there is no continuous electrically conductive path in ACAs before bonding. During bonding, the component terminations are pressed against the corresponding pads on the substrate, compressing the conductive particles trapped between the component terminations and substrate pads in order to form the electrically conductive path. After bonding the ACAs become electrically conductive in the vertical direction and remain insulating in the x-y plane. The junction schematic of ACA is shown in Figure 5. High heat and pressure are required in the ACA bonding process. ACAs are usually used to bond fine pitch, high I/O count flip chip and TAB devices. In recent years, ACAs have also been used to bond flexible cable and LCD display driver chips. Since there is no flux involved in the assembly process, the use of ECAs is a no-clean process. The ECAs also work well with all types of board finishes.

2.3.2 Percolation and Formation of Conductivity in ICA

The conductivity of isotropic conductive adhesive depends on the uniform dispersion of conductive fillers and formation of a conductive path by the fillers in the polymer. In this case, percolation theory is most frequently used to describe the transition from insulator to conductor.

According to Kirkpatrick and Zallen's model for spherical shaped particle fillers, the minimum volume fraction for the fillers is 16%. This number corresponds with most traditional metal filled conductive adhesives, which require 25% to 30% volume fraction to overcome the percolation threshold and ensure the electrical conductivity. [8] However, for less than 1% volume fraction of carbon black in the resin can cause electrical conduction. This is because when the particles are dispersed in the liquid and size of the dispersed phase particles is between 1nm and 1µm in at least one dimension, the theory of colloids is also needed to describe the interaction among the dispersed particles. There are two interaction forces to be considered in this case. One is repulsive coulombic force caused by electrostatic charging of particles. The other is the London-van der Waals force

of attraction. The coulombic force can cause a potential energy barrier. To form a conductive network, the potential energy barrier has to be surmounted by inducing agglomeration. Thermal energy alone may be insufficient to surmount the potential energy barrier. Adding external shear force or increasing the ionic concentration can help overcome the potential energy barrier. It is reported by Ruediger et al. [10] that at 0.9% volume fraction, the thermal activation energy provided by curing leads to network formation. By applying low shear force the threshold can be reduced 0.3% volume fraction. By increasing ionic concentration the threshold can be reduced to 0.06% volume fraction.

2.4 Carbon Nanotubes

Carbon nanotubes are a new form of carbon, first identified in 1991 by Sumio Iijima of NEC, Japan. [11] It is an exciting new material with potential to make significant impacts in the fields of sensors, electronic devices, composites, and many other areas. Carbon nanotubes are sheets of graphite rolled into seamless cylinders. In graphite, each carbon atom is evenly connected to three other carbon atoms in the xy plane and a weak π -bond exists in the z axis. The sp² hybridization happens in the graphite and forms hexagonal lattice sheet of graphite. The p_z orbital causes van der Waals interaction between sheets of graphite. The free electrons in the p_z orbital moving within this cloud are not localized to any single carbon atom and are responsible for graphite's electrical conductivity. [12] In carbon nanotubes, the delocalized π -electrons not only can conduct electricity but also can be used to attach functionalized groups to the carbon nanotubes through π - π stacking interactions.

Besides having single wall nanotubes (SWNTs), nanotubes can also have multiple walls (MWNTs)--cylinders inside the other cylinders. The carbon nanotube can be 1-50nm in diameter and 10-100µm in length, with each end "capped" with a half fullerene dome consisting of five and six member rings. Along the sidewalls and cap, additional molecules can be attached to functionalize the nanotube to adjust its properties. Carbon

nanotubes possess many unique and remarkable properties (chemical, physical, and mechanical), which make them desirable for many applications.

2.4.1 Structure and properties of Carbon Nanotube

SWNTs have different properties depending on chirality. The chiral vector $R = na_1$ + ma₂ is used to describe this characteristic, where a₁ and a₂ are unit vectors in the twodimensional hexagonal lattice, and n and m are integers. The Armchair line is the line across each hexagon, separating them into two equal halves. If R lies along the Armchair line (=0°), then it is called an "Armchair" nanotube. If the wrapping angle between R and armchair equals 30°, then the tube is of the "Zigzag" type. Otherwise, if the wrapping angle between R and armchair is larger than 0° but smaller than 30°, then it is a "chiral" tube. The vector a_1 lies along the "Zigzag" line. The direction of a_2 is a reflection of a_1 over the Armchair line. When added together, they equal the chiral vector R. All armchair tubes are metallic. Chrial and Zigzag tubes are either metallic or semiconducting depending on the chiral vector integers, n and m. When the chrial vector n-m=3q, where q is an integer, the carbon nanobute is expected to be metallic, while all others are semiconducting. It can be estimated 1/3 of all carbon nanotubes are metallic. [13] Krishnan, Dujardin et al. reported the measured Young's modulus of SWNT is 1.25×10^3 GPa. [14] Hone, Whitney et al. reported the measured peak thermal conductivity of SWNT is 6000 W/m·k, three times that of diamond. [15]

MWNTs consist of several concentric layers of rolled up graphite sheets. The distance between each layer is approximately 0.34 nm, slightly larger than the interlayer distance of graphite sheets and the layers are coupled to each other through van der Waals forces. [16] MWNTs are always electrically conductive and Kaneto, Tsuruta et al. reported the measured electrical conductivity of MWNT is 1000-2000 S/cm. [17] Kim, Shi et al. reported the measured thermal conductivity of MWNT is 900 W/m·k at room temperature [18] and the thermal conductivity decreases with increasing defect rate of MWNT.

2.4.2 Synthesis and Purification of Carbon Nanotubes

There are a number of different methods to synthesize carbon nanotubes. Among these synthesis methods, arc discharge, laser vaporization and chemical vapor deposition (CVD) are dominant.

Arc discharge method

The carbon arc discharge method was initially used to produce C_{60} fullerenes and MWNTs were found as a by-product by Sumio Iijima in 1991. In this method, two carbon electrodes are placed end to end in a reactor filled with inert gas (usually helium or argon) and electrical arcing is used to vaporize the surface of one rod and form deposits on the other electrode. [19] This technique produces a mixture of multiple components including amorphous carbon, fullerenes and fused MWNTs. Large quantities of MWNTs per run can be produced by this method, however the yield of MWNTs is around 25% and further purification is need to remove amorphous carbon, fullerene and catalytic metals. SWNTs can be found in arc discharge products too. However the yield of SWNT is too low for large-scale production. [20] [21] Laser vaporization is usually used to synthesis SWNTs.

In 1997 Journet et al. managed to use arc discharge method for large scale production of SWNT by using a specific mixture of catalytic metals. It suggests that the growth mechanism for SWNTs is more depending on the catalysts and less dependent of the synthesis method. [22]

Laser vaporization method

In 1996 Thess and Lee et al. produced SWNT yields of more than 70% by condensation of a laser-vaporized carbon-nickel-cobalt mixtures at 1200°C. The SWNTs produced by this method are nearly uniform in diameter and self-organize into "ropes" with single-rope conductivity larger than 10^4 S/cm at room temperature. [23] Different SWNT average diameters and lengths can be achieved by changing growth temperature,

catalyst composition, and other process parameters. Both arc discharge and laser vaporization methods depend on vaporization. Carbon nanotubes formed in vaporization methods are highly entangled with each other and mixed with unwanted amorphous carbon and metals. Thus they are difficult to purify and manipulate.

Chemical Vapor Deposition

In CVD methods, hydrocarbons serve as the gaseous carbon source. They decompose and the carbon atoms deposit on the metal catalyst particles to form carbon nanotube. Both SWNT and MWNT can be produced by CVD. The morphology of carbon nanotubes varies with the different catalyst (such as cobalt, nickel, iron or mixture of metals) and feed-gas (such as acetylene, ethylene or mixture of methane and hydrogen). At the University of Kentucky's Center of Applied Energy Research, Andrews et al. developed a low-cost bulk production CVD method to produce high purity and well aligned (unentangled) MWNTs. The ferrocene-xylene mixture is used as feed-gas and iron nanopaticles are used as the catalyst. In the reaction, the ferrocene-xylene mixture decomposes at temperatures in the range 625-775 °C and at atmospheric pressure, iron nanoparticles are nucleated and begin to deposit carbon (from xylene and ferrocene) as well-aligned pure MWNT arrays on the quartz surfaces. [24]



Figure 1: Comparison of wedge bonding and ball bonding



Figure 2: Structure of TAB polymer tape




Figure 3: Structure of ILB (a) and OLB (b)



Figure 4: Bump forms for flip chip: (a) solder bump, (b) plated stub bump, (c) wire stub bump, (d) adhesive bump



Figure 5: Junction schematic of ACA

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Chapter3 Model of MWNT/epoxy Composite

3.1 Electrical conductivity of Epoxy/MWNT composite

Solid materials can be grouped into three categories by the electrical conductivity: insulator, semiconductor and metal. The conductivity of the material is decided by the electronic energy level structure. The electrons in the solid crystals are arranged in energy bands separated by band gap (Figure 6). The highest occupied band in an insulator or semiconductor is called the valence band and the lowest unoccupied band is called the conduction band. Only when electrons are excited to the conduction band can current flow in these materials. In insulator, the band gap between valence band and conduction band is large, so only few electrons in the valence band can access the conduction band. Thus the electrical conductivity is low. In semiconductor the band gap between valence band and conduction band is small than in insulator. Therefore the electrical conductivity of semiconductors is comparably larger than insulator. Additional electrons in semiconductors can cross the band gap by exposing the material to electrical field or thermal excitation. Therefore the conductivity of a semiconductor is generally intermediate, but varies widely under different conditions. In metals the conduction band overlaps with the valence band and no band gap exists. Therefore metals have very high conductivity. Usually the conductivity of an insulator is below 10^{-7} S/cm, semiconductor is between 10^{-7} to 10^{-2} S/cm and metal is above 10^{2} S/cm at room temperature.

Pristine polymers have intrinsically large energy band gaps, thus are good insulators. Typical conductivity of an epoxy is less than 10⁻¹⁴ S/cm. In commercially available metal filled conductive adhesives, highly conductive metal particles are mixed with insulating polymer matrix to form electrically conductive composites. At low filler loading levels, the conductivity of the filler/polymer composite is very low (close to the intrinsic conductivity of the polymer) and does change with increasing filler loading. When the volume fraction of conductive filler in the polymer system exceeds the critical volume fraction (percolation threshold), a three-dimension network is established by the conductive filler particles and the conductivity of the composite increases dramatically by several orders of magnitude. The sudden increase in conductivity resulting from a small

increase in loading is called the critical range. The relation between the conductivity of the composite and the volume fraction of loading can be described by the scaling law in equation (1), in which p is volume fraction of filler, p_c is the critical volume fraction (percolation threshold) and t reflects the dimensionality of the system. When the volume fraction of filler exceeds the critical region, all the filler particles are involved in at least one conductive path and conductivity increases slowly with further increase in filler loading. Figure 7 illustrates the curve of volume resistivity as a function of filler loading in metal filled ICA.

$$\sigma \propto (p - p_c)^t \tag{1}$$

In conductive adhesives, there are three major factors affecting the conductivity of the composite: intrinsic conductivity of the filler particles, dimension (aspect ratio) of the filler particles and the contact resistance between the particles. MWNTs with small size and high aspect ratio can form more contacts than large metal particles with the same weight percent loading. MWNTs therefore form conductive networks in the composite more readily in than the spheres or flakes and the percolation threshold of MWNTs/epoxy composite is expected to be extremely low.

When the conductive fillers in the composite have formed a percolated network, the resistance of the composite is determined by the intrinsic conductivity of the filler particles and the contact resistances between the filler particles. The contact resistance (R_c) consists of two factors. One is the constriction resistance (R_{cr}) and the other is tunneling resistance (R_t).

$$R_c = R_{cr} + R_t \tag{2}$$

When two conductive filler particles contact with each other, constriction resistance is caused by constriction of electron flow through the small contact area. R_{cr} is proportional to the intrinsic resistivity of the conductive filler particles and inversely proportional to the diameter of the contact spot.

Quantum-mechanical tunneling takes place when the distance between two conductive fillers in the composite is small (in the order of 100 Å or less). R_t is proportional to the distance between the conductive filler particles and the work function of the filler particle, and is independent of the resistivity of the polymer film between the particles. In general, the tunneling resistance dominates the contact resistance in conductive adhesives. [25] The schematic of the resistance model in each percolated linkage in shown in Figure 8, in which R_i is the intrinsic resistance of the conductive filler particles.

3.2 Mechanical strength of Epoxy/MWNT composite

The strength of an adhesive to bond different surfaces depends on its ability to wet the surfaces and the bonding mechanism.

Wettability

Adhesives need to effectively wet the surfaces to be joined to form strong bond. Wettability, defined as the ability for an adhesive to wet a surface, is essential in maximizing the coverage on the different surfaces and minimizing the voids in the bond lines. It is measured by the equilibrium contact angle, θ , shown in Figure 9.

All materials in the solid or liquid state have energy associated with their surfaces. The energy arises from the unsaturated bonds on the surface. This surface energy depends on the surface characteristics of the material and the surface energy of the surrounding medium. For a drop of adhesive wetting the metal pad, as shown in Figure 9, the surface energy of the solid-vapor interface is denoted by γ_{sv} . The surface energy of the liquid-vapor interface is denoted by γ_{sv} . The surface energy of the refore denoted by γ_{sl} .

The wettability for the adhesive on the metal pad depends on the relative magnitudes of the surface energies for the adhesion and the metal pad. The balance of the surface tension can be described in the following Young's equation. A lower contact angle θ between the adhesion drop and the solid implies better wetting.

$$\gamma_{sl} + \gamma_{lv} \cos \theta = \gamma_{sv} \tag{3}$$

Wetting occurs when the surface tension of the liquid adhesive is close to or slightly less than the surface tension of the substrate. As liquids, adhesives have high surface tension, which require high surface tension of the bonding surface to produce low contact angle and good wettability. The roughness of the surface can also affect the wettability. If the contact angle θ is larger than 90°, then increasing the surface roughness degrades the wettability. If the contact angle θ is smaller than 90°, then increasing surface roughness improves wettability and adhesion.

Besides surface tension, there are two additional issues need to be addressed in formulating adhesives, especially for two-part epoxy adhesive. One issue involves the rheology and pot life. The pot life of the two-part epoxy is usually less than 48 hours after mixing the two parts together. After exceeding the pot life, the adhesive becomes partly polymerized and the viscosity of the adhesive increases dramatically. In this case, the adhesive will no longer wet the surface. Thus stable and long pot life polymer is preferred in formulating the MWNT filled adhesive. The other issue needs to be considered is the excessive wetting and bleedout problem. When either the resin or the curing agent has a much greater wettability than the other, the two parts will separate from each other and migrate over the intended boundary on the PCB pad.

Bonding mechanism

There are several bonding mechanisms for polymer adhesives: direct chemical bonding, hydrogen bonding and mechanical interlocking. More than one bonding mechanism could be involved in the adhesion between two surfaces.

Direct chemical bonding usually happens between the polymer adhesive and plastic laminated substrate board, where strong covalent bonds can form during the curing process. For inorganic or metal interfaces, adhesion promoters (silane coupling agents) are needed to form chemical bridges between the polymer and the surface. Adhesion promoters having two or more functional groups can form strong chemical bonds with the adhesive on one end and chemically bond to the ceramic or metal surface at the other end. Adhesion promoter is often used to coat the metal filler particles in metal filled epoxy conductive adhesives to enhance adhesion to the resin matrix. Hydrogen bonding occurs between hydroxyl groups in epoxy and oxide groups or hydroxyl groups of metal oxides on metal surfaces. For mechanical interlocking, a low viscosity liquid or paste fills the porous surfaces or encapsulates the peaks and valleys of a rough surface. In this case more surface area is exposed compared to a smooth surface. The epoxy in our MWNT/epoxy adhesive may form strong bonds with the metal pads by hydrogen bonding. However there are no strong bonds between the MWNT filler and the epoxy resin matrix.

3.3 Thermal conductivity of Epoxy/MWNT composite

Neat epoxies are thermal insulators with thermal conductivity usually less than 0.2 W/m·K. Method 5011 of MIL-STD-883 specifies the minimum thermal conductivity for electrically conductive adhesive is 1.5 W/m·K. The thermal conductivity of epoxy can be improved by mixing with metal particles or other thermal conductive fillers. Similar to the percolation threshold phenomenon in electrical conductivity, the thermal conductivity of the epoxy only increases modestly with increased filler loading until reaching a critical volume fraction and above which the thermal conductivity increases rapidly. However even with high loading of filler particles, the thermal conductivity of the composite is still far below the bulk thermal conductivity of filler itself. The thermal conductivity of commercially available metal filled epoxy conductive adhesives is usually ranging between 1.7 W/m·K to 8 W/m·K. By mixing diamond particles with epoxy, thermal conductivity as high 11.5 W/m·K can be achieved. The thermal conductivity of a two-

phase composite can be modeled by Lewis and Nielsen model. [26] So the Lewis and Nielsen model is used to model the thermal conductivity of MWNT filled conductive adhesive.

$$\kappa = \kappa_c \frac{1 + AB\phi_f}{1 - B\phi\phi_f} \tag{4}$$

$$\phi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right) \phi_f \tag{5}$$

$$B = \frac{\kappa_f - 1}{\kappa_f + A} \tag{6}$$

Where κ_c is the thermal conductivity of the continuous phase (epoxy)

 κ_f is the thermal conductivity of the filler

A is the shape parameter that increases with aspect ratio

 ϕ_f is volume fraction of filler, and

 ϕ_m is the packing factor (maximum filler level while maintaining the continuous matrix phase).

In our MWNT/epoxy composites, MWNTs can be considered as three dimensional randomly dispersed rods or fibers. According to L. E. Nielsen's research the value of ϕ_m for rods or fibers packed in three dimensional random networks is 0.52. [27] The packing factor for MWNT/epoxy composite can be set as 0.52, however, there is no reference value for A due to the ultra-high aspect ratio of MWNTs. The measured thermal conductivity values of MWNT/epoxy composites will be used to evaluate the shape parameter of MWNTs in Chapter 5.



Figure 6: Schematic for the band gap of metal, semiconductor and insulator



Figure 7: Volume resistivity vs. filler loading



Figure 8: schematic of resistance model in percolated linkage



Figure 9: equilibrium contact angle, θ

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Chapter4 MWNT/EPOXY COMPOSITE PREPARATION

4.1 MWNT Dispersion and Mixing

Due to the large surface area of MWNTs, the van der Waals attractive force between MWNTs is extremely large and the as-produced MWNTs tend be the state of entanglement and close packing. Thus the first challenge in the formation of conductive network in the polymer matrix is the uniform dispersion of MWNTs.

To disperse MWNTs into epoxy, either mechanical methods or chemical methods can be used. Mechanical methods include ultrasonication and high shear mixing. High energy ultrasonication has been used to disperse MWNTs into polymer/solvent solution with low viscosity. [28] However long duration high-energy ultrasonication has the potential to cause defects and breakage of MWNTs. High shear mixing method can uniformly disperse MWNTs into polymers with a small but acceptable amount of tube breakage. [31] The chemical methods include using surfactant to alter the surface energy of MWNTs without adding covalent bonding to the MWNT surface and functionalization of MWNTs to improve the compatibility with polymer. Using surfactant is preferred in electrical application because of the possibility of dispersing MWNTs without disturbing the movement of free electrons on the surface of the MWNTs. However, adding surfactant induces plasticization effect to the polymer matrices and compromises the improvement in mechanical properties caused by embedded of carbon nanotubes. [29] [30] Functionalization of MWNTs out-layer usually compromises the electrical properties. Therefore it is more often used in applications focusing on mechanical properties. The procedure for making MWNT/polymer structural composites usually includes dispersing MWNTs into organic solvent by adding nonionic surfactant and then mixing with the polymer. Ultrasonication is often used as well to help dispersing.

In preliminary experiments, a two-part epoxy purchased from Miller-Stephenson Chemical Company, Inc,. Epon® Resin 862 and EPI-CURE® 3234 curing agent (triethylene tetramine) was mixed at a ratio of 100:15.4 by weight. Resin 862 is a bisphenol F – epichlorohydrin based epoxy resin (CAS # 28064-14-4). MWNTs used in this experiment were obtained from the University of Kentucky Center for Applied Energy Research (CAER) with average lengths of 50 μ m and average diameters of 20 nm yielding an aspect ratio of approximately 2500. The chemical vapor deposition growth conditions are described in reference [24]. Figure 10 shows SEM images of as-produce MWNTs peeled off from substrate.

To compare the hand mixing and ultrasonication mixing methods, MWNT/epoxy composites with 0.4 wt% MWNT loading were prepared by both methods. Figure 11 (a) and (b) are fracture cross section SEM images for MWNT/epoxy composites without and with ultrasonication process. It can be seen that MWNTs are more uniformly dispersed with ultrasonication process. For the same loading, the measured resistance for the sample made by ultrasonication process is much smaller than the sample made by hand mixing, which also indicates the better dispersion of MWNTs with ultrasonication process.

In the ultrasonication method, MWNTs were first added into EPI-CURE 3234 because the viscosity of Resin 862 was too high for effective dispersion while the viscosity for EPI-CURE 3234 is much lower and MWNTs can disperse evenly with the help of ultrasonic energy. After 30 minutes in an ultrasonic bath, a good mixture of MWNT and EPI-CURE 3234 was achieved. The MWNT/EPI-CURE mixture was added into Resin 862 and mixed by hand to make the conductive adhesive. Figure 12 (a) and (b) are microscopy images of MWNT/epoxy composite and commercially available 63Sn/37Pb solder on metal pad. It can be seen that the MWNT/epoxy composite has similar wetability to the metal pad as melted solder. However MWNT/epoxy composite wets not only the metal pad but also the organic board material. Additional dam material may be needed for MWNT/epoxy composite in SMT assembly process to avoid short-circuit problems. Since the viscosity of the mixture changes dramatically as a function of MWNT loading, 0.4 wt% loading is the highest loading that can be mixed effectively by the ultrasonic method for this epoxy composition. A short pot life of only 20 minutes for this epoxy was also observed.

To further increase the loading of MWNT, a lower viscosity resin, Resin 815C, and the same curing agent were used in the second set of experiments. Resin 815C is a modified bisphenol A – epichlorohydrin based epoxy resin (CAS # 25068-38-6). The resin is produced by the condensation reaction of epichlorohydrin and bisphenol A with N-butyl glycidyl ether (CAS # 2426-08-6) added to adjust the resin viscosity. The ratio of Resin 815C to EPI-CURE 3234 is 100:12. Besides changing the resin, the CNTs were added into Resin 815C rather than the curing agent because the viscosity of Resin 815C is low enough for the CNTs to be dispersed evenly with the help of ultrasonic mixing. After a half hour in an ultrasonic bath, the curing agent was added into the mixture of resin and CNTs to make the conductive adhesive. By using this low viscosity resin, up to 1 wt% of MWNTs can be dispersed in the epoxy composite. Adding additional n-butyl glycidyl ether (BGE) as thinner and γ -glycidoxypropyltrimethoxysilane as adhesion promoter to further reduce viscosity of the composite, up to 2 wt% loading can be achieved. However these additives can cause excess outgasing problem in the curing process and degrade electrical and mechanical performance, thus makes it difficult to characterize the properties of MWNT/epoxy composite. The short pot life problem still exists in this sample preparation method.

In the ultrosonication method previous experiments, two parts of the epoxy were manually mixed after disperse CNTs into one part of the epoxy. Above 0.8 wt%, it is difficult to achieve an even mixing and remove the air bubbles trapped in the samples. To further increase the CNT loading and achieve better mixing result, a planetary mixer (AR-250, Thinky Inc., Japan) was used to disperse the MWNTs into the epoxy resin. The planetary mixer generates large continuous centripetal forces (up to 400G) by compound motion of the revolving centrifuge and the counter-rotation of the material container. The principle of its operation is that large, continuous centrifugal force produced by combination of the rotation of the material while blending them. The revolution speed in mixing mode and de-foaming mode is 2000 rpm and 2200 rpm. The rotation speed in mixing mode and de-foaming mode is 800 rpm and 60 rpm. The high shear mixing action achieves uniform distribution and removes air bubbles from the mixture in a short

amount of time. No blending tool is required and each batch is mixed in a new clean container to prevent contamination. To counteract the short pot life, a new formulation of epoxy was used. Resin was changed back to diglycidyl ether bisphenol-F (Epon 862, Shell Chemical, USA) for its good adhesion and strength. The curing agent was change to a slow cure agent, methyl hexahydro phthalic anhydride (MHHPA, Miller-Stephenson Chemical, USA). Cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN, Shikoku Chemical, Japan) was used as catalyst. With this combination of epoxy system, all the chemicals and the MWNTs can be mixed in one process and the observed pot life is more than 72 hours.

4.2 Curing kinetics of MWNT/epoxy composite

Differential scanning calorimetry (DSC) was used to determine the curing kinetics for the prepared MWNT/epoxy composite. In DSC analysis, difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Heat generated by the sample material is compared to the heat generated in a reference material as the temperature of both materials is raised at the same rate. As-produced MWNTs mixed were into bisphenol-F based epoxy resin and curing agent (MHHPA) by planetary mixing. The uncured MWNT/epoxy composite was used sample material. An empty pan was used as reference. DSC (Q-100, TA Instruments, USA) heats the sample and reference from room temperature to 250 °C at the heating rate of 10 °C/min. The samples were placed in hermetic aluminum DSC pans and scanned in a nitrogen purge gas. The curing profiles for 2 wt%, 4 wt% and 8 wt% loadings of MWNT/epoxy composites and neat epoxy are shown in Figure 13, Figure 14, Figure 15 and Figure 16 respectively.

The peak in the curve corresponds to the curing of the composite. The onset temperatures of the peak for different loadings of MWNT/epoxy composites and neat epoxy are very close (all between 146 °C to 148 °C). The same onset temperature for both

composites results from using the same epoxy and curing agent system. So the merchant recommended curing condition for the epoxy was followed. All the MWNT/epoxy composite samples in later experiments were cured at 150 °C for 30 minutes.

4.3 Shatter Milled MWNT

Besides the as-produced MWNT from CAER, short MWNTs were also prepared to evaluate effect of MWNTs with different size (aspect ratio) on the properties of MWNT/epoxy composite. Shatter milled short MWNTs were prepared by grinding the MWNT in a shatter mill for 10 minutes. Figure 17 and Figure 18 are transmission electron microscope (TEM, JEOL 2010F, Japan) images showing that MWNT can be broken and tips opened by shatter milling. Figure 19 and Figure 20 are TEM images demonstrating that the average length of shatter milled MWNT is less than 5 µm.



Figure 10: SEM image of as-produced MWNT



а



b

Figure 11: SEM images for comparison of dispersion: (a) 0.4 wt% of MWNT dispersed in epoxy without ultrasonication, (b) 0.4 wt% of MWNT dispersed in epoxy with ultrasonication.





b

Figure 12: Microscopy images for comparison of wetting: (a) cured MWNT/epoxy composite on copper pad, (b) reflowed commercially available 63Sn/37Pb solder on copper pad



Figure 13: curing profile for 2 wt% loading of MWNT/epoxy composite



Figure 14: curing profile for 4 wt% loading of MWNT/epoxy composite



Figure 15: curing profile for 8 wt% loading of MWNT/epoxy composite



Figure 16: curing profile for neat epoxy



Figure 17: Broken shatter milled MWNT



Figure 18: Open-ended shatter milled MWNT



Figure 19: TEM micrograph of shatter milled MWNT



Figure 20: TEM micrograph of shatter milled MWNT

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Chapter5 Experiments and Results Discussion

5.1 Volume Resistivity Measurement

The electrical conductivity of a conductive adhesive is often evaluated as the volume resistivity (ohm-cm) of the material. For bulk material, volume resistivity can be measured by the method shown in Figure 21. In Figure 21, the bulk material is placed between the two electrode plates. A digital ohmmeter is connected to the two electrode plates and reading is taken once the display stabilized. Volume resistivity can be calculated using the following formula:

$$R_{vol} = R \frac{l \cdot w}{t} \tag{7}$$

where

 R_{vol} = volume resistivity (ohm-cm)

R = measured resistance (ohm)

l = length of the electrode plate (cm)

w = width of the electrode plate (cm)

t = thickness of the conductive adhesive (cm)

To measure the volume resistivity, the mixed epoxy/MWNT composites can be either injection molded to make in bar shape and use the method discussed above or printed as a film and use four-point probe method. In our experiment, MWNT/epoxy composites were stencil-printed onto aluminum oxide substrates (4 inches \times 4 inches, CoorsTek, USA) to form uniform film samples. On the stencil pattern were five 1 cm \times 1 cm square openings and two substrates were printed for each epoxy/MWNT loading, thereby ten squares for each loading were printed. Samples were held at 80 °C for 4 hours to out gas and then cured at 150 °C for 30 minutes. The volume resistivity of each sample was calculated by multiplying the sheet resistance by the average thickness of the epoxy/MWNT composite layer.

A four-point probe tester (Signatone, USA) was used to record the voltage drop

with the injected current. The sheet resistance (R_s) is proportional to the ratio of the voltage, V to the current, I.

$$R_s = C \cdot \frac{V}{I} \tag{8}$$

C=4.53 (for infinite film)

A stylus profilometer(Alpha-Step 500, Tencor, USA) was used to scan each square in four directions to achieve the average thickness, t. Figure 22 illustrates the volume resistivity measurement sample and arrows indicate scan directions for stylus profilometer thickness measurements. The sheet resistance was converted to volume resistivity, ρ_v by multiplying by thickness, t (in cm). Volume resistivity for each of the ten squares was calculated and averaged to determine the volume resistivity for each loading.

$$\rho_{\nu} = 4.53 \times \frac{V}{I} \cdot t \tag{9}$$

5.1.1 Relation between MWNT loadings and volume resistivity

To evaluate the relationship between the MWNT loadings and the volume resistivity of the composite, the as-produced MWNT obtained from CAER were mixed into Epon 862 (resin), MHHPA (curing agent) and 2E4MZ-CN (catalyst) epoxy system by using high shear planetary mixer. Table 1 shows measured volume resisvitivy of epoxy/MWNT composites with different loadings. Figure 23 plots volume resistivity as function of the MWNT loading. In Figure 23, the largest reduction in volume resistivity at 0.25 wt% is observed, which means the MWNTs start forming interconnected path before the loading reaches 0.25 wt%. Thus the percolation threshold is less than 0.25 wt%. In preparing all the samples, it was observed that the viscosity of the samples increases with increasing MWCNT loading. Above 12 wt% as produced MWCNT, the epoxy/MWCNT composite becomes too viscous to process by screen printing, stencil printing or pressure dispensing.

In Figure 23, it can be seen that the volume resistivity decreases with increasing

MWNT loading and above 2 wt% volume resistivities are close to each other. The 8 wt% sample has almost the same resisvity as the 12 wt% sample, which means the epoxy is saturated after 8 wt%. Based on Figure 23, it can also be determined that the percolation threshold of MWNT/epoxy is lower than 0.25 wt%. The ratio of MWNT density vs. epoxy density is about 2:1, so the corresponding percolation threshold of volume fraction is about 0.125 vol%. Comparing with the percolation threshold of 20 vol% to 25 vol% for metal filler particles in ICAs, the percolation threshold for MWNT in epoxy is ultra-low. This is consistent with the analysis in the electrical conductivity model analysis in Chapter 3. However highest conductivity achieved in our MWNT/epoxy experiments is on the order of 10^{0} S/cm, which is not as high volume conductivity of commercially available metal filled ICAs (usually above 10^3 S/cm). To investigate if the volume resistivity of epoxy/MWCNT composite is dominated by the epoxy layer on the surface of epoxy/MWCNT composite, SEM micrographs were taken for the top and cross-section of MWNT/epoxy composite with 4 wt% loading. To get the cross-section micrograph, volume resistivity sample was put in liquid nitrogen and broken by impact to expose the fracture surface and maintain the structure of MWNTs in the cross-section.

Figure 24 and Figure 25 show SEM micrographs of the top surface and fracture cross-section, respectively. From the top surface micrograph (Figure 24), it is difficult to determine whether MWNTs are exposed on the top surface of the composite. By comparison, in Figure 25, randomly dispersed MWNT can be seen protruding from the fracture cross-section. To further determine if the resistance of the epoxy/MWCNT composite is mainly caused by the lack of exposing MWNT to the surface, argon plasma (Plasma-Preen II862) was used to etch the epoxy layer on the surface of epoxy/MWCNT composites. The argon airflow rate was 3 cubic feet per minute and power was 900 watts. Figure 7 is the SEM micrographs for the epoxy/MWNT composite surface after plasma etching for 8 minutes. Volume resistivity measurement samples for 8 wt% MWCNT loading were exposed in argon plasma for 4, 8 and 16 minutes. A four-point probe tester was used to evaluate the voltage drop with the same current injected. After 4 and 8 minutes of argon plasma etching, no change in the four-point probe voltage reading was observed. After etching for 16 minutes, the voltage reading was reduced by an average

number of 4%. No measureable change in thickness was detected by the surface profiler, therefore the decrease in volume resistivity of the epoxy/MWNT composite due to plasma etching can only be estimated as 4%. Based on the four point probe and SEM analyses, etching the thin epoxy surface layer on the bulk epoxy/MWNT surface only slightly improves the volume resistivity value and it can be concluded that the volume resistivity of epoxy/MWNT composite is not dominated by the epoxy layer on the surface of epoxy/MWNT composite.

To explain the combination of ultra-low percolation threshold and moderate electrical volume conductivity, the components in the conductivity model discussed in Chapter 3 needs to be examined more closely. For each percolated linkage inside the epoxy, the resistance is determined by the intrinsic conductivity of the filler particles and the contact resistances between the filler particles.

The intrinsic conductivity of MWNTs is on the order of 10^3 S/cm [17] while the conductivity of silver, the most commonly used filler in metal filled ICAs, is 6.3×10^5 S/cm. [32] Consequently, the intrinsic resistance of the filler particles in MWNT/epoxy composite is larger than a commercially available ICA.

The contact resistance (R_c) consists of two factors, the constriction resistance (R_{cr}) and the tunneling resistance (R_t). The R_{cr} is proportional to the intrinsic resistivity of the conductive filler particles and inversely proportional to the diameter of the contact spot. The intrinsic resistivity of MWNT is 10^2 times larger the intrinsic resistivity of silver particles. Therefore the constriction resistance between filler particles is much larger for MWNT than silver particles due to larger intrinsic resistivity and smaller size of the contact area (smaller diameter of contact spot).

The tunneling resistance R_t is proportional to the distance between the conductive filler particles and work function of the filler particle. The work function of silver is 4.3 eV [32] while the work function of MWNT is 4.95 eV. [33] Therefore the tunneling

resistance between filler particles is larger for MWNT than silver particles as a result of both the higher work function and lower volume loading (larger inter particle spacing) of the MWNT. In compositions where the polymer matrix shrinks during the curing process, a certain amount of pressure is applied to the metal filler particles by the matrix which decreases the distance between the metal particles and increases the diameter of the contact spot. However, the shrinkage of the matrix during curing of the MWNT/epoxy composite does not move the MWNTs as much due to lack of crosslink bonding between MWNTs and epoxy. Therefore the contact resistance between MWNTs in the cured MWNT/epoxy composite is much larger than the contact resistance between silver particles in the cured silver filled ICA. For each percolated linkage in MWCNT/epoxy composite, the intrinsic conductivity of the filler particle is smaller than the silver filled ICA. Hence epoxy/MWNT composites in our experiments (less than 6 vol%) have higher resistivity than commercially available metal filled ICAs (above 25 vol%) although the percolation threshold of MWCNT in epoxy is much lower than that of metal.

5.1.2 Relation between aspect ratios of MWNT and volume resistivity

To evaluate the relationship between the size of MWNTs and the volume resistivity of the MWNT/epoxy composite, different loadings of MWNT with varying sizes into bisphenol-F based epoxy by high shear planetary mixer. MWNTs of varying lengths and diameters were obtained from CAER and Cheap Tubes, Inc.. Table 2 lists the description of the test samples starting with the largest aspect ratio MWNT in Group A. MWNT in Group E were shatter milled MWNT from Group A with lengths in 1-5 μ m and average diameter of 20 nm. In Group D, samples were made by mixing MWNTs used in Group A and Group E at a 1:1 ratio.

Table 3 shows the measured volume resistivity for different loadings of MWNT with different aspect ratios. In Table 3, it can be observed that at the same weight percent loading (3 wt%, 4 wt%, 5 wt%), the volume resistivity decreases with increasing MWNT

aspect ratio. The change in resistivity indicates that the longer MWNT are more likely to make contact with each other to form an electrical path. In preparing all the samples, it was observed that at the same loading, the viscosity of the samples increases with increasing MWNT aspect ratio. However for Sample D, the combination of long and short MWNTs, shows low volume resistivity (comparable with Sample A) and moderate to low viscosity (lower than Sample B and Sample C but higher than Sample E). It demonstrates a possible compromise for both the electrical performance and processing requirements.

5.1.3 Resistivity for the mixture of long and short MWNTs

To evaluate the effect for the ratios of the long and short MWNT mixture on volume resistivity, as-produce long MWNT and shatter milled short MWNT were both obtained from CAER and mixed into bisphenol-F based epoxy by high shear planetary mixer. The total weight percent of as-produced MWNT and shatter milled MWNT was set at 12 wt%, and measured volume resistivity for different ratios of as-produced and shatter milled MWNT were compared. The aspect ratio of as-produced MWNT is less than 250.

In Table 4, "a" represents as-produced MWNT and the "s" represents shatter milled MWCNT. In preparing samples, it was observed that at the same weight percent loading, epoxy/MWNT composites made with shatter milled MWNT and combinations of long and short MWNT have much lower viscosity than the composites made with only as-produced MWNT. The maximum loading of only shatter milled MWNT can be mixed into epoxy is approximately 36 wt%. At higher loadings, the viscosity is too high for printing or dispensing. With 36 wt% loading of shatter milled MWNT, the measured volume resistivity of epoxy/MWNT composite is 11.96 Ω -cm. From Table 2, it can be determined that MWNT with high aspect ratio form electrically conductive paths more easily than MWNT with low aspect ratio. This experiment result can be explained by the conductivity model discussed in Chapter 3. For each percolated linkage in the composite,

the linkage formed by long MWNTs has less contact resistance. For the same loading, the MWNT/epoxy composite contacting more long MWNTs has a smaller volume resistivity. However better processability and dispersion can be achieved by replacing a portion of long MWNTs with short MWNTs, thus improving the conductivity. Mixing high and low aspect ratio MWNT can achieve a good compromise of both the conductivity and processability.

5.2 Contact resistance measurement

To measure the contact resistance of MWNT filled ICAs, daisy chain patterns were etched on 1-ounce copper clad FR-4 printed circuit board (PCB) (D&L Products, USA) and 1206 size zero-ohm resistors (DigiKey, USA) were assembled onto the daisy chains. 10 zero-ohm resistors comprise each daisy chain with 4 daisy chains on each board. A multimeter (HP 3478A, USA) was used to measure the resistance for each daisy chain on the test board. The mean value of each daisy chain was calculated and divided by 20 to get an average contact resistance for each set of 10 resistors.

To evaluate the relationship between the loadings of MWNT and the contact resistance, as-produce MWNT from CAER are mixed into bisphenol-F based epoxy by high shear planetary mixer. Figure 27 shows the result for the contact resistance measurement for 2, 4 and 8 wt% MWNT loadings. It can be seen that the value of contact resistance and standard deviation both reduce with increasing MWNT loading but still fairly large for electronic applications. It was observed that pressure on the components during curing effectively reduces the contact resistance. By applying pressure during curing, contact area is enlarged while the height between pads is reduced so that more contact points between pads and MWNT are achieved, thus reduce the contact resistance.

5.3 Scattering Parameters Measurement

RT/duroid 5880 (Rogers, USA) high frequency board was used to etch Sparameter measurement test vehicles. Microstrip lines were patterned on the 1 ounce copper double-side high frequency board. Zero-ohm resistor was attached across the two microstrip lines by using the MWNT/epoxy composite, commercially available silver filled ICA (80 wt% silver loading, Epoxy Tech., USA) and solder. To prepare the MWNT/epoxy composite, as-produce MWNT from CAER are mixed into bisphenol-F based epoxy by high shear planetary mixer. A network analyzer (HP 8753D, USA) was used to measure the S-parameters for this test pattern in the frequency range of 50 MHz to 3 GHz. Measured S-parameters for solder joints, commercially available Ag filled ICA and epoxy/MWCNT composites with different MWCNT loadings were compared. The schematic of the test vehicle is shown in Figure 28.

Figure 29 and Figure 30 show the comparison of measured scattering parameters S11 (input reflection coefficient) and S21 (forward transmission coefficient) for solder joints, epoxy/MWNT composites and silver filled ICA. S11 and S21 are the input reflection coefficient and forward transmission coefficient of the 50 Ω terminated outputs. It can be concluded that MWNT filled ICAs have comparable AC performance to tin-lead solder and commercially available silver filled ICA in this configuration and frequency range.

5.4 Lap Shear Test

To evaluate the mechanical degradation of the polymer matrix caused by adding MWNT, a lap shear test was conducted by using an Instron 4442 tensile tester (Instron, USA). The test sample was prepared by attaching two copper clad printed circuit board tabs using the epoxy/MWNT composite. The lap area was 0.25 inch \times 0.25 inch. Figure 31 illustrates the test sample. The amount of adhesive dispensed on the contact area was controlled by using a pressure dispenser. The tensile tester grips the 1×1 inch tabs and pulls until the composite attached lap area fails. The break force was recorded and divided by the lap area to calculate the lap shear strength (Psi). 8 samples were prepared to determine the average lap shear strength for each loading of MWNT. Tabs were milled
from bare printed circuit boards using a MITS FP-21T milling machine. To prepare the samples, tabs were attached by MWNT/epoxy composite and commercially available silver filled ICA.

Samples made by 2 wt%, 4 wt% and 8 wt% loadings of MWNT respectively were used to compare the relationship between the loadings of MWNT and the lap shear strength of the MWNT/epoxy composite. To evaluate the effect of ratios for the long and short MWNT mixture on lap shear strength, as-produce long MWNT and shatter milled short MWNT were both obtained from CAER and mixed into bisphenol-F based epoxy by high shear planetary mixer. The total weight percent of as-produced MWNT and shatter milled MWNT was set at 12 wt%, and measured lap shear strength for different ratios of as-produced and shatter milled MWNT were compared.

Figure 32 shows the comparison of lap shear strength for MWNT/epoxy composites and commercially available silver filled ICA (80 wt% silver loading, Epoxy Tech., USA). Generally MWNT/epoxy composites can retain more lap strength of the epoxy due to less degradation of the epoxy system as a result of the low volume percent loading. By comparison, it can be seen that higher lap shear strength was achieved with lower loadings. For the same total weight percent loading, the mixtures of long and short MWNTs yielded increasing lap shear strength with decreasing proportion of long MWNTs.

5.5 Die Shear Test

Die shear testing is usually used to determine the adhesion strength between the semiconductor die and the package substrate. In this test, the whole assembly is tightly fastened, force parallel to the substrate is gradually applied on the edge of the die, the break force is measured for each die-substrate assembly and the type of failure is determined by visual examination of the residual. Mil-Std-883 Method 2019 is the most widely-used die shear test standard. To conform to this test standard, the following requirements for the test equipment must be fulfilled. First, the tool contacting the die

should uniformly distribute the force to the full length of an edge of die. Second, the contact tool must be perpendicular the die attach plan. Third, a rotational substrate holding fixture is needed to ensure the die edge and contact tool are parallel. Forth, a binocular microscope (10X min magnification) and lighting system is needed to observe the die and contact tool interface while the test is being performed. The direction of the applied force must be perpendicular to the die edge and parallel to the substrate plane. The contact tool must only contact with the die edge and avoid contacting the die attach material or the substrate. There are three die separation modes: the die cracks and die residual remains, die separates from the die attach material and die attach material separates from the substrate. Schematic of the die shear test is shown in Figure 33

In our experiments, there are 32 copper pads on each test board. 4 wt% loading of MWNT was mixed into bisphenol-F based epoxy by high shear planetary mixer. The MWNT/epoxy composite was dispensed on the pads by using air pressure dispenser. A manual pick and place machine was used to attach the silicon dies onto the copper pads. The assembly was cured at 150°C in a thermal oven. The silicon die size is 0.06 inch \times 0.05 inch = 0.003 inch². According to the standard, twice the minimum strength for 30×10^{-4} inch² is 2.5Kg. However the lowest measured shear strength for our preliminary test is 5.184 Kg. Thus the adhesion strength for all of our samples satisfies the Mil-Std-883 standard requirements. The standard deviation of 2.086 indicates large variance in the die shear strength. It comes from the variance in the amount of composite being dispensed each time by the pressure dispenser and could be improved by using a stencil printer to dispense the composite instead of pressure dispenser.

5.6 Thermal Conductivity Measurement

Thermal conductivity κ is defined as the quantity of heat, ΔQ , transmitted during time Δt through a thickness L, in a direction normal to a surface of area A, due to a

temperature difference ΔT , under steady state conditions and when the heat transfer is dependent only on the temperature gradient. The typical unit is W/(m·K).

$$\kappa = \frac{\Delta Q}{\Delta t} \times \frac{L}{A \times \Delta T} \tag{10}$$

Giving the specific heat (c_p) capacity, bulk density (ρ) and thermal diffusivity (α) values, thermal conductivity (κ) can be calculated by the following formula:

$$\boldsymbol{\kappa} = \boldsymbol{\alpha} \cdot \boldsymbol{c}_p \cdot \boldsymbol{\rho} \tag{11}$$

Thermal diffusivity

Thermal diffusivity (α) was measured by the laser flash apparatus (Netszch, USA) in the CAER. The architecture of this equipment is shown in Figure 34. This equipment uses a thermo-analytical method, which measures the thermal diffusivity of the sample at constant temperatures while monitoring the temperature increase of the sample caused by the absorbed energy of a laser flash. Pure epoxy and epoxy/MWNT composites with different MWNT loadings were cured in a Teflon die 0.5 inch in diameter and a diamond saw cut 0.06 inch thick discs to make the test samples. Thermal diffusivity of samples at different temperatures were measured and compared.

To evaluate the relationship between the MWNT loadings and the diffusivity of the MWNT/composite, as-produce MWNT from CAER are mixed into bisphenol-F based epoxy by high shear planetary mixer. Samples with 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% loadings are measured and compared with neat epoxy. Figure 35 shows the measured thermal diffusivity of neat epoxy and epoxy/MWNT composites. At the same temperature, the thermal diffusivity increases with increasing MWNT loading. For the same loading, the thermal diffusivity decreases with increasing temperature.

To further evaluate the effect for the ratios of the long and short MWNT mixture on thermal diffusivity, as-produce long MWNT and shatter milled short MWNT were both obtained from CAER and mixed into bisphenol-F based epoxy by high shear planetary mixer. The total weight percent of mixed MWNTs was set at 12 wt%, and measured thermal diffusivities for mixed MWNT/epoxy composites, and pure asproduced MWNT/epoxy composites were compared. The measured results are shown in Figure 36. The measured values of thermal diffusivity for 4 wt% and 8 wt% of pure asproduced MWNT/epoxy composites confirm that the larger MWNT loading is the higher thermal diffusivity is. From the measured value for mixed as-produced and shatter milled MWNT/epoxy composites, it can be seen that at the same temperature, the thermal diffusivity increases with increasing long MWNT ratio in the mixture. These results confirm that for the same loading, the larger long MWNT ratio in the mixture, the less high interfacial thermal resistance existing in the thermal conduction network in the composite.

Specific heat capacity

Specific heat capacity (C_p) is a mass normalized measure of the energy required to raise the temperature of a material. It can be measured by heating a test normalized for sample mass and heating rate and recording the heat flow.

$$C_p = \frac{EQ}{RM} \tag{12}$$

Where C_P = Specific Heat Capacity

E = DSC Calibration Factor

Q = Heat Flow

R = Heating Rate, and

M =Sample Mass.

When using conventional DSC to measure, C_p is generally calculated from the difference in heat flow between a blank run and sample run under the identical heating rate and heating conditions.

$$C_p = K_{Cp} \times \frac{Q(sample) - Q(blank)}{R}$$
(13)

Where $K_{Cp} = C_p$ cell calibration constant.

Modulated DSC (MDSC) differs from conventional DSC in that it applies two simultaneous heating rates to the sample. The linear or average heating rate provides the same information (total heat flow rate) as standard DSC, while the sinusoidal (modulated) heating rate is used to determine the fraction of the total heat flow rate that responds to a changing heating rate. In general, this heat flow rate is caused by heat capacity (C_p). This fraction of total heat flow is called the reversing heat flow or the heat capacity component of the total heat capacity. Heat flow does not respond to the changing heating rate is called non-reversing heat flow or the kinetic (time-dependent) component. The relationship between MDSC signals can be described in the following equation

$$\frac{dH}{dt} = C_p \times \frac{dT}{dt} + f(T,t)$$
(14)

Where dH/dt = total heat flow rate (mW or mJ/s)

 C_p = sample heat capacity (J/°C); specific heat capacity × sample mass dT/dt = heating rate (°C/min), and f(T, t) = heat flow that is function of temperature and time (mW).

Total heat flow has two components. One is reversing heat flow, $C_p \times dT/dt$, which is a function of applied heating rate (dT/dt). The other is non-reversing heat flow, f(T, t), which is a function of time at an absolute temperature. The limitation of standard DSC is that it measures only the sum of these two components. MDSC can determine not only the total heat flow but also the two individual components. C_P is determined by dividing the modulated heat flow amplitude by the modulated heating rate amplitude.

$$C_{p} = \frac{HeatFlowAmplitude}{HeatingRateAmplitude} \times K_{Cp}$$
(15)

Where $K_{Cp} = C_p$ cell calibration constant.

The measured thermal conductivity for 8 wt% MWNT/epoxy composite is shown in Figure 37. It can be seen that heat capacity increases with the increasing temperature. For 8 wt% MWNT/epoxy composite, the measured heat capacity at room temperature is 1.024 J/g·C. From Figure 36, the measured thermal diffusivity for 8 wt% MWNT/epoxy composite at room temperature is 0.34 mm²/sec. The measured density is 1.2 g/cm³. So the calculated thermal conductivity for 8 wt% MWNT/epoxy composite at room temperature is approximately 0.42 W/m·K. It can be concluded that the improvement in thermal conductivity for the epoxy is limited even though MWNT individually have an ultra high thermal conductivity. Two factors contributing to the low thermal conductivity are the lack of significant contact area between MWNTs dispersed in the matrix and that heat is not effectively transferred by tunneling. As a result, the epoxy works as a thermally insulating layer between the MWNT. For the Lewis and Nielsen model discussed in Chapter 3, at room temperature the thermal conductivity for the two-phase composite (κ) is 0.42 W/m·K, the thermal conductivity of the filler (κ_f) is 900 W/m·K [18], thermal conductivity of the continuous phase (κ_c) is 0.2 W/m·K, volume fraction of filler (ϕ_f) is 0.04 (4 vol%) and the packing factor (ϕ_m) is 0.52. The shape parameter (A) can be calculated by taking κ , κ_c , κ_f , ϕ_f , ϕ_m into equation (4), (5) and (6) in Chapter 3. The calculated value of A is 26.8. In L. E. Nielsen's research, the values of A for randomly oriented rods with aspect ratio of 2, 4, 6, 10, 15 are 1.58, 2.08, 2.8, 4.93, 8.38 respectively. The average aspect ratio of MWNTs used in this experiment is around 2500. Comparing with the calculated value of shape factor for MWNTs, it can be concluded that when MWNTs are considered as randomly dispersed rods or fibers, the calculated value of A is consistent with the rule that A increases with increasing filler's aspect ratio.

5.7 Glass Transition Temperature Measurement

Glass transition temperature T_g of the cured sample was derived from the curve of reversible heat flow versus temperature by using DSC. Results of 2 wt% and 8 wt% samples were shown in Figure 38 and Figure 39. It can be seen that the measured T_g for these two loadings are approximately the same and corresponds to the T_g on the data sheet of the epoxy. It can be concluded that the glass transition temperature of MWNT/epoxy composite is determined by the epoxy system and independent of MWNT loadings in this range.

5.8 Accelerated aging test

The cured volume resistivity sample for 4 wt% MWNT/epoxy composite was aged in the environmental chamber (AH-202XS, Bryant) under the aging condition of 85 °C/85% RH. The volume resistivity was measured every 24 hours. Figure 40 shows the volume resistivity shift vs. time for 4 wt% MWNT/epoxy composite in the 85 °C/85% RH accelerated aging test. It can be seen that the volume resistivity of MWNT/epoxy slightly decreases after exposing to the heat and moisture. Usually the volume resistivity for the cured metal filled conductive adhesive increases when subject to heat and moisture due to the galvanic corrosion of the metal content. The shift in resistance can be reduced by adding corrosion inhibitor. The volume resistivity of our sample does not increase without adding corrosion inhibitor because MWNTs are corrosion resistant to the heat and moisture. The slight decrease in the volume resistivity could result from water entering the epoxy matrix and water has a lower electrical resistance than epoxy.

Loading (wt%)	Volume resistivity Standard deviation	
0	1×10^{14}	-
0.25	1.57×10^{5}	-
0.5	1.92×10^4	-
1	534.09	-
2	65.21	7.32
4	9.55	0.81
8	2.16	0.30
12	2.17	0.27

Table 1: Measured volume resistivity for epoxy/MWNT composites with different MWNT loadings

Sample	MWNT Source	MWNT Dimensions	MWNT Aspect Ratio
А	CAER	average length: 50 µm	≅2500
		average diameter: 20 nm	
В	Cheap Tubes	length: 10-30 µm	≅250-1500
		diameter: 20-40nm	
С	Cheap Tubes	length: 10-20 µm	< 200-400
		diameter: >50 nm	
D	CAER	MWNTs in sample A and	2500 + 50-250
		sample E mixed at 1:1 ratio	
E	CAER	lengths: 1-5 µm	≅50-250
		average diameters: 20 nm	

Table 2: MWNT aspect ratios for volume resistivity samples

Loading	Volume resistivity (Ω-cm)				
(wt %)	А	В	С	D	E
0	1×10 ¹⁴	1×10 ¹⁴	1×10 ¹⁴	1×10 ¹⁴	1×10 ¹⁴
0.25	1.57×10^{5}				
0.5	1.92×10^4				
1	534.09				
2	65.21				
3	14.18	158.16	198.16		
4	9.55	83.32	102.17		
5	6.29	45.05	50.05	8.35	2.2×10^4
6	3.50				

Table 3: Volume resistivity for different loadings of MWNT with different aspect ratio

Sample		Loading (wt%)	Volume resistivity (Ω-cm)
А	a	12	2.17
	S	0	
В	a	10	0.96
	S	2	
С	a	8	2.05
	S	4	
D	a	6	5.07
	S	6	
Е	a	4	7.48
	S	8	
F	a	2	24.17
	S	10	
G	a	0	149.45
	S	12	

Table 4: Volume resistivity of epoxy mixed with different ratios of long and short MWNT



Figure 21: Method for measuring bulk volume resistivity



Figure 22: Sample design for volume resistivity measurement



Figure 23: Log (ρ) volume resistivity versus MWNT loading for as-produced high aspect ratio MWNT in epoxy



Figure 24: SEM micrograph for top surface



Figure 25: SEM micrograph of cross-sction



Figure 26: SEM micrograph for 8 wt% MWNT/epoxy composite after argon plasma etching for 8 minutes



Figure 27: Contact resistance measurements at 2, 4 and 8 wt% loading of as-produced MWCNT in epoxy cured with applied weight



Figure 28: Schematic of the high frequency test board



Figure 29: Input reflection coefficient (S_{11}) for solder, silver filled adhesive and MWCNT filled epoxies from 50 MHz to 3 GHz



Figure 30: Forward transmission coefficient (s_{21}) for solder, silver filled adhesive and MWCNT filled epoxies from 50 MHz to 3 GHz



Figure 31: Lap shear test sample



Figure 32: Comparison of lap shear strength for silver filled ICA and various ratios of asproduced and shatter milled MWNT in epoxy



Figure 33: Schematic of die shear test



Figure 34: Structure of LFA



Figure 35: Laser flash thermal diffusivity analysis for as-produced MWNT/epoxy composite and neat epoxy



Figure 36: thermal diffusivity analysis for mixed MWNT/epoxy composites and pure asproduced MWNT/epoxy composites



Figure 37: Measured heat capacity for 8 wt% MWNT/epoxy composite



Figure 38: DSC analysis showing T_g for 2 wt% MWNT/epoxy composite



Figure 39: DSC analysis showing T_g for 8 wt% MWNT/epoxy composite



Figure 40: volume resistivity in accelerated aging test

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Chapter6 Conclusion and Future Work

The research done in this dissertation investigated the potential of replacing the metal filler particles in conductive adhesives with MWNTs to make a conductive adhesive with high electrical and mechanical performance as well as light weighted, lead-free and corrosion resistant properties. To formulate the MWNT filled conductive adhesive, different epoxy systems, loadings, dispersing methods and combinations of MWNTs with different size were tested. Electrical conduction, mechanical adhesion and thermal conduction mechanism for the MWNT/epoxy composite were analyzed. Experiments were designed to measure the electrical, mechanical and thermal properties and assess the reliability. Preliminary accelerated aging tests show a slight decrease in volume resistivity as a result of 85/85 exposure.

The results of this work indicate that epoxy/MWNT composites have a significantly lower percolation threshold than metal filled ICA although the achieved highest conductivity is lower than metal filled conductive adhesive. The percolation threshold is determined by the aspect ratio of MWNTs. The electrical conduction mechanism in the epoxy/MWNT composite is influenced by intrinsic conductivity of the MWNT and the contact resistance between MWNT. The contact resistance is determined by shrinkage of the matrix, distance between particles and the work function of the MWNT. Consequently, the contact resistance and volume resistivity are not yet comparable to commercially available metal filled ICAs. AC scattering parameters measured for MWNT/epoxy composites are competitive with solder and silver filled ICA.

Replacing metal fillers in ICA with MWNT improves the lap shear strength and the strength to weight ratio due to the low loading and weight of MWNT. Thermal conductivity of 8 wt% MWNT/epoxy composite at room temperature is about twice of that for neat epoxy although the intrinsic thermal conductivity of MWNT is thousand of times greater than neat epoxy. In the Lewis and Nielsen model for two-phase composites, the MWNTs can be considered as three-dimensional randomly dispersed rods or fibers.

In preparation for the samples, several resins, curing agents, catalysts and solvents were evaluated to adjust the rheology and pot life. Hand mixing, ultrosonication and high shear mixing methods were compared to disperse the MWNTs. Pot life of 72 hours and uniform dispersion was achieved by using the latest formula and high shear mixing method. Varying the fractions of long and short MWNT in the composite improves both the volume resistivity and processability of the mixture. The adhesive samples were also tested for their compatibility with current electronic packaging techniques. The MWNT filled conductive adhesives are compatible with pressure dispensing, stencil printing and oven curing process.

Based on current results, there are a number of possible directions to extend this research. These directions include:

- Use MWNT treatment to change surface morphology or add functional groups to the out layer of MWNTs so that strong bond can be formed between MWNTs and the polymer matrix.
- Purify or select highly conductive MWNTs to further improve electrical conductivity.
- Investigate the compatibility for MWNT filled conductive adhesives with different PCB pad surface finishes.
- Investigate the potential of using shatter milled MWNT filled conductive adhesive as electromagnetic interference (EMI) shielding or electrostatic discharge (ESD) protection coating material.
- Further evaluate the reliability of this adhesive subject to heat and moisture. Investigate the potential application in corrosive environment
- Investigate the potential of integration this conductive epoxy in PWB manufacturing to make light weighted, mechanically strong metal free PWB.

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