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TASK 1.4
Comparison and trade-off of existing TIM and interconnect alternatives

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WORK PACKAGE 1 : SYSTEMS AND APPLICATIONS SPECIFICATIONS

TASK 1.4
Comparison and trade-off of existing TIM and interconnect alternatives

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1 ABBREVIATION / DEFINITION

TIM	Thermal Interface Material
SOI	Silicon On Insulator
CNT	Carbon Nano Tube
BLT	Bond Line Thickness
MCM	Multi-Chip Module
LCC	Life Cycle Cost
SCM	Single-Chip Module
Rth	Thermal Resistance
HNC	Hierarchical Nested Surfaces
SWCNTs	Single-Walled Carbon NanoTubes
MWCNTs	Multi-Walled Carbon NanoTubes
CVD	Chemical Vapor Deposition

2 THERMAL INTERFACE MATERIALS – STATE OF THE ART RESEARCH

2.1 INTRODUCTION

The integration and power density of microelectronics products has been continuous increasing for decades. Efficient systematic thermal management solutions are an immediate requirement to dissipate the large amount of heat generated by the integrated chips and other components. Thermal interface materials play a key role for the heat dissipation at all levels within a microsystem. The function of TIMs is to fill the microscale gaps between two contacting materials to enhance the heat conduction through the interfaces. It has been widely recognized that thermal interface materials are one of the main bottlenecks preventing the efficient heat transfer from the integrated chips to the heat sinks and ambient environment. It is believed that the performance of conventional thermal interface materials can no longer support the quick development of the microelectronics industry. Intensive efforts have therefore been put into the research of novel thermal interface materials in both academia and industry during recent years. Some well-delivered reviews on TIM technologies with different focuses are provide by Dani [1], Dean [2], Gowda [3], Prasher [4], Samson [5], and Sarvar [6].

This document provides a comprehensive review of the recent progress of research work performed to develop new thermal interface materials. The review starts by classifying existing thermal interface materials and analyzing their advantages and disadvantages. Seven main classes of materials are examined, including thermal grease, thermal gel, phase change materials, phase change metallic alloys, thermally conductive adhesives, solders, thermal tapes and pads. The state-of-the-art research is then reviewed with an emphasis on those materials based on various carbon allotropes, such as graphite, carbon nanotubes and carbon fibers. The carbon based materials are widely considered as one of the most promising approaches in this field due to the high thermal conductivity of carbon allotropes. The barriers to achieve high performance and wide application of these materials are also discussed. A variety of methods to theoretically study the materials and to evaluate their performance are also generally examined.

2.2 EXISTING THERMAL INTERFACE MATERIALS

It has been a long history of using and developing thermal interface materials in the IT industry. A variety of technological approaches have been developed and applied to meet different needs in all kinds of applications. Thermal interface materials can generally be classified into seven different categories: thermal grease, thermal gel, phase change materials, phase change metallic alloys, thermally conductive adhesives, solders, thermal tapes and pads [2, 5]. The typical composition, general properties, advantages and disadvantages of each category are summarized in Table 1. Representative commercial available materials with high performance are also listed for every category.

It should be noted that the selection of a suitable thermal interface material is highly dependent on the application and should be considered based on not only the thermal performance but also on the reliability issues, mechanical and electrical properties, etc. The market of thermal interface materials has developed to a remarkable size and keeps expanding rapidly.

Material Class	Description	Advantages	Disadvantages	Typical Composition
Grease	Grease matrix with high thermally conductive ceramic or metallic particle fillers.	- High thermal conductivity - Low assembly pressure - No cure required (re-usable) - No delamination - Low cost	- Pump out and phase separation - Dry out - Migration	- Silicone compound matrix - AlN, BN, Al_2O_3 or Ag fillers
Gel	Cross-linkable polymer matrix with high thermally conductive ceramic or metallic particle fillers.	- Good thermal conductivity - Conforms to surface irregularities before cure - No pump out or migration - Low cost	- Cure required - Possible delamination - Lower thermal conductivity than grease - Lower adhesion than adhesive	- Curable silicone or olefin compound matrices - AlN, BN, Al_2O_3 or Ag fillers
Phase Change Material	Matrix undergoes phase change to liquid state below material operating temperature. Commonly contains metallic or ceramic filler particles.	- Stable and less susceptible to pump out - No cure required - No delamination	- Requires attach pressure - Lower thermal conductivity than grease - Potential voiding	- Polyolefin, epoxy, polyester or acrylic matrices - AlN, BN, Al_2O_3 or Ag fillers
Phase Change Metallic Alloy	Low melting point metallic alloy undergoing phase change to liquid state below material operating temperature.	- High thermal conductivity - No cure required - Re-usable	- Intermetallic growth at interfaces - Oxidation and corrosion - Potential voiding - High cost	- In - In/Ag - Sn/Ag/Cu - In/Sn/Bi
Adhesive	Curable adhesive matrix filled with thermally conductive ceramic or metallic particle fillers.	- High thermal conductivity - Conforms to surface irregularities before cure - No pump out or migration - Provides mechanical attachment	- Cure required - High modulus (CTE stress may induce crack or delamination)	- Epoxy matrix - Ag filler
Solder	Metal alloys for reflow.	- Provides mechanical attachment - High thermal conductivity - Easy to handle - No pump out	- Requires reflow - High modulus (CTE stress may induce crack or delamination) - Not re-usable - Intermetallic growth at interfaces - Oxidation and corrosion - High cost	- In - In/Ag - Sn/Ag/Cu - In/Sn/Bi
Tape	Reinforced polymer matrix with thermally conductive ceramic or metallic particles	- Provides mechanical attachment - Easy to handle - No pump out or migration - No cure required - Easy to handle - Low cost	- Low thermal conductivity - High thermal surface resistance	- Silicone compound matrix - Fiberglass reinforcement - AlN, BN, Al_2O_3 or Ag fillers
Pads	Elastomeric material with high thermally conductive ceramic or metallic particles.	- No pump out or migration - No cure required - Low cost - Easy to handle	- Low thermal conductivity - High thermal surface resistance - High assembly pressure - Not re-usable	- Silicone compound matrix - AlN, BN, Al_2O_3 or Ag fillers

Table 1: Common thermal interface material classes and their respective key properties.

2.3 STATE OF THE ART RESEARCH

Several trends can now be clearly observed in the field of thermal interface material research. One trend is that a big fraction of the research work focuses on the novel types of high thermally conductive fillers, including carbon allotropes and ceramics. Another important trend is to extend the study on TIMs down to a much smaller scale than before. This not only deepens the understanding in this field but also provides a possibility to create and modify micro- and nano-scale structures to vary the material properties and improve the performance.

Thermal interface materials based on the carbon allotropes diamond, graphite, amorphous carbon, the buckminster fullerene and the carbon nanotube have recently attracted massive interest within the research community. The obvious rationale behind this is the high thermal conductivity offered by the carbon allotropes and in certain cases the cost versus performance ratio. A few good papers about the carbon nano structures and their thermal properties are provided in references [7-9]. Other kinds of fillers with high thermal conductivity, such as silicon carbide, boron nitride, aluminum nitride, aluminum oxide, silver and other metals, have also been extensively studied. The distribution and alignment of the thermally conductive fillers are also important factors. For example, thermal conductivity enhancement with aligned CNTs is claimed to be at least 3 times of that with randomly distributed CNTs according to the calculation [10]. Another example is that bimodal distribution of conductive particles is found to produce better thermal properties [11, 12]. Table 2 gives an overview of the recent related research works, listing the materials structures, fabrication methods, test methods, results, and so on. The table is divided into two parts: TIMs with carbon-based fillers and those filled with other materials.

Besides the massive work on developing novel thermal interface materials, research work are also performed in other aspects of TIM technology. Solder-based TIMs and phase change materials are studied in some big companies, such as Intel [68], IBM [69], and Honeywell [70, 71]. Theoretical research of TIMs based on analytical, statistical and numerical methods is also performed intensively. Some examples can be found in [10, 41, 72-78]. The modeling and simulation of TIMs using molecular dynamics or finite element method is also executed [79-82]. Difficulties still exist in direct linking of theoretical calculation, modeling and simulation to the experimental work. However these studies are very important as valuable guidance and assistance to the experimental research. It’s also worthwhile to mention the research on small scale structures within TIMs, such as voids and contacts [83-87].

Table 2 : Summary of recent research works on thermal interface materials

TIMs with carbon-based fillers

Reference	Material Structure	Fabrication Method	Test Method	Results	Notes
[13]	VA-MWNT	Dendrimer-assisted PECVD	PA	8-18 Kmm^2/W	
[14]	SWNT-epoxy, 1wt%		Comparative method	k: 70%↑@40K, 125%↑@RT	
[15]	SWNT-PMMA, 7%		Double guarded plate	k: 55%↑	
[16]	VA-MWNT-PDMS	TCVD	Laser flash	1.8-3.8 W/mK	2-4 times larger across the alignment direction
[17, 18]	VA-MWNT	PECVD	ASTM D5470	25 Kmm^2/W	“lift-off” transfer of CNT film
[19]	VA-MWNT-Cu	TCVD, Electroplating of Cu	ASTM D5470	20 Kmm^2/W	In vias
[20]	A-SWNT-epoxy, 3 wt%	Magnetic field processing	Comparative method	4-6 W/mK	
[21]	MWNT-poly(α-olefin) oil, 1 vol%		Transient hot wire	k: 150%↑	
[22]	VA-SWNT/MWNT/CNF	TCVD/PECVD		R: 60%↓	Comparative study of 5 systems
[23]	VA-MWNT	PECVD	PA	Si-CNT-Ag : 15.8 Kmm^2/W	

				Si-CNT-CNT-Cu : 4.0 Kmm^2/W	
[24, 25]	VA-MWNT-Cu	PECVD	PA	10 Kmm^2/W	Cu foil coverd by MWNT films on both sides
[26]	SWNT-epoxy, 2.3 wt%	HiPCO, infiltration	Comparative method	0.61W/mK, 3.8 W/mK (calculation)	
[27]	CB/SWNT/DWNT/MWNT/etc.-epoxy		Hot Disk	max 0.25 W/mK	Comparative study of different fillers at different filler content
[28, 29]	VA-MWNT	PECVD	3-omega	74-83 W/mK @ 295-323 K	
[30]	VA-DWNT	TCVD	IR	3.8×10^{-4} Km^2/W	CNT-CNT interface
[31]	VA-MWNT-PDMS	CVD, inject molding	ASTM D5470	1.21 W/mK	
[32]	Graphite nanoplatelet-epoxy, 1vol%		Transient hot wire	0.20-0.23 W/mK (200-300K)	
[33]	SWNT	HiPCO	Transient absorption	Interface thermal conductance G ≈ 12 MWm^2/K	Simulation also included
[34]	SWNT-LC, well ordered			4.8 W/mK	
[35]	Diamond-Epoxy (10-60 wt%)		Laser flash	0.3-1.2 W/mK	
[36]	CNT/PDMS, 3.8wt%	CVD, grinding	ASTM D5470	k: 65%↑	

[37]	Graphite			12.2 W/mK	
[38]	MWNT/SWNT-epoxy		Hot Disk	Very little enhancement	
[8, 39]	VA-CNF-Cu	PECVD, electrodeposition	ASTM D5470	0.25 Kcm^2/W	
[40]	VA-SWNT	PECVD	Thermorelectance	1.2×10^{-5} Km^2/W	Pd/Al evaporated on the surface
[41]	VA-MWNT	TCVD	Xenon flash	~300% enhancement for Al and graphite pieces	Theoretical study also included
[42]	VA-MWNT	TCVD	Xenon flash	8 W/mK (calculated value)	
[43]	Graphite sheets-polymer		ASTM D5470	5.66 W/mK	
[44]	VA-MWNT	TCVD	PSTTR	Bonded interface conductacnd: 9.0 ×10^4 W/m^{2}K, one magnitude higher by a thin In layer	
[45]	VA-MWNT	TCVD	ASTM D5470	12 Kmm^2/W	Cu foil coverd by MWNT films on both sides
[46]	MWNT-HDPE, 38vol%		Laser flash	Two time higher thermal diffusivity	
[47, 48]	VA-MWNT-PDMS	TCVD	ASTM D5470	0.43 W/mK, 1.52 and 0.83 Kcm^2/W for MWNT film with and without Al layer	

[49]	VA-MWNT	PECVD	IR		
[50]	VA-MWNT	PECVD	IR	CNT: 19.8 Kmm^2/W CNT-PCM: 5.2 Kmm^2/W	
[51]	SWNT-epoxy		ASTM C518 (LaserComp FOX50)	0.9 W/mK	Purity of the SWNTs affects k dramatically
[52]	MWNT(2wt%)/CB(10wt%)-epoxy		ASTM E1461 (Anter FlashLine 3000)	MWNT-epoxy: 0.5 W/mK CB-epoxy: 0.6 W/mk	
[53]	VA-MWNT	TCVD	ASTM D5470	28 Kmm^2/W	
[54]	VA-MWNT	TCVD	ASTM D5470	15 Kmm^2/W	
[90]	CNF-filled thermal grease			1.25 W/mK	Commercially available
[91]	A-CF-filled adhesive film			750 W/mk	Commercially available

TIMs with other fillers

Reference	Material Structure	Test Method	Results	Notes
[55]	Ag-epoxy/thermoplastic, 77-93 wt%, 28-62 vol%	Laser flash	3-60 W/mK, bondline 1-10 W/mK	Anisotropy of k: ~1.5, 3 layer analysis: effect of contact resistance
[56]	Al$_2$O$_3$-PS, 10 wt%	Laser flash	0.18 W/mK	
[57]	Al$_2$O$_3$-Epoxy, 50 wt%	Guarded heat flow meter	Single mode: 0.35-0.65 W/mK, bimodal: 0.38-0.4	Bimodal. k reduced by adding nanoparticles

			W/mk	
[58]	BN/Al_2O_3/TiB_2/SiC-epoxy	Laser flash	3.9-13.5 W/mK	
[59]	BN-Epoxy, 30wt%		0.6-0.9 K/W, 1.2-1.6 K/W	
[11]	BN-polybenzoxazine	Laser flash	1.5-32.5 W/mK	Bimodal distribution
[60]	AlN/BN/AlN+wollastonite/AlN+SiC-HDPE	ASTM C1113 (Mathis Instruments TC Probe)	0.75-3.66 W/mK	Adding wollastonite/SiC slightly enhances k
[35]	SiO_2(3 µm)/Al_2O_3(0.3 µm)/BN(1 µm)-Epoxy, 10-60 wt%	Laser flash	0.5-1.0 wt%	
[61]	BN/AlN-PBT, 0-25 vol%	Laser flash	0.4-0.8 W/mK, max 1.1W/mK	
[62]	Ni-epoxy, 0-30 vol%	Laser flash	2.0 W/mK	High Tg (220-250 ℃)
[12]	AlN-Epoxy, 60-74 vol%	ASTM E1530 (ULVAC GH1)	4.0-8.2 W/mK	Bimodal distribution
[63]	AlN(particles/whiskers)/AlN+SiC-PVDF, 40-60 vol%	Laser flash	1.3-11 W/mK	
[64, 65]	SiC(0.2 µm)/SiC(0.2 µm)+Ni(5 µm)-Epoxy	Heat flow meter (Kyoto Electronics QTM500)	0.5-0.6 W/mK	
[66]	BN(0.5-15 µm)-HDPE, 0-35 vol%	Hot Disk	0.8-1.2 W/mK	
[67]	BN(0.3-20 µm)-Silicone	Laser flash	0.5-1.2 W/mK	

[92]	Micro-&nanofibers-In alloy	ASTM D5470	~8 W/mK	

Abbreviations: **A-:** aligned-, **CB:** carbon black, **CF:** carbon fiber, **CNF:** carbon nanofiber, **DWNT:** double-walled nanotube, **HiPCO:** High-Pressure CO Conversion, **IR:** infrared, **MWNT:** multiwalled nanotube, **PA:** photoacoustic, **PECVD:** plasma-enhanced chemical vapor deposition, **SWNT:** single-walled nanotube, **TCVD:** thermal chemical vapor deposition, **VA-:** vertically aligned-

2.4 ANALYSIS, DISCUSSIONS AND SUMMARY

Thermal interface materials have become a popular research topic in recent years, drawing attention from not only material scientists, but also chemists, physicists, and many researchers in other fields. There are a few reasons behind the popularity of TIM research. One driving force is the urgent necessity of novel high performance materials from the industry. The discovery and great achievements of high thermally conductive nano- structures, especially carbon nanotubes and nanofibers, form another obvious reason.

It can be clearly seen from the discussion in previous sections and summarily table that the majority of recent research works is focused on the development of thermal interface materials with carbon fillers, among which carbon nanotube is the most chosen filling material. Noteworthy players in the field of carbon-based TIM development include research groups from Purdue University [6, 23-25, 49, 50], Hongkong University of Science and Technology [17-19], and Tsinghua University [31] etc. The research work performed at Purdue University is noticeable due to the various growth methods of CNTs and test approaches applied in TIM development. At Hongkong University of Technology, interesting works on “lift-off” transfer of CNT film and development of CNT-Cu composite have been performed. Unique approach of making CNT-PDMS composite by inject molding has invented at Tsinghua University.

Despite the massive research work, these new thermal interface materials still only exist in laboratories and are far away from real application. The performance of most these novel TIMs is still not high enough to overtake the current high-end commercial products. Many of them even generate lower results compared to commercial materials. Several technical barriers can be identified. Although theoretical predictions show that carbon nanotubes have extremely high thermal conductivity, these computations are all based on CNTs with assumed perfect atomic structures, which are very difficult to achieve by current technology. The experiments works reporting high measurement thermal conductivity values of CNT are normally performed using short and single CNTs. It’s reasonable that these values are much higher than those results measured for CNT films or composites. Moreover, the contact thermal resistances between nanotubes and other substances, e.g. the polymer matrix in composites and the substrates above or below the CNT films, are very high and cause the low overall performance of the materials. Another main technical barrier is the high difficulty of achieving high filling ratio and dense alignment of CNTs in the TIMs. In the case of using CNTs as fillers of composites, it is hard to obtain good dispersion of CNTs and high filling ratio. In the case of aligned CNT films, the gaps between nanotubes in the films are indeed quite large compared to their diameters, causing a rather low effective filling content.

Besides the research works on carbon nanotube-based thermal interface materials, some other novel approaches are also worthwhile to mention. Namics develops a kind of thermal conductive adhesive by adding nano particles to improve the heat transfer, achieving the thermal conductivity as high as 7 W/mK. Btechcorp claims they successfully developed a TIM consisting of very densely filled vertically aligned carbon fibers with a dramatically high thermal conductivity of 750 W/mK [91]. The high volume production of these materials is still questionable. At Chalmers University of Technology, a unique kind of TIM with micro- and nanofibers as reinforcement and solder alloys as fillers has been invented, obtaining good thermal properties and possibly low manufacturing cost and difficulty [92].

Another important problem in this field is the difficulty to evaluate and compare the results from different sources. Many similar experiments produce far different results. It is partly due to the different preparation methods of materials. A more important reason is probably that the materials are tested by many different methods. A variety of implementations are applied even using the same method or standard. A sound discussion about this issue can be found from Lasance’s papers [88, 89].

High performance thermal interface materials are an important necessity in the IT industry to enable the higher density integration of electronics systems and further downscaling of components. This reported summaries and analyzed the current status of TIM research and development. It's pointed out that the modification of the materials at micro- to nano- scale is the key to achieve great progresses. The main technical barriers in material development and difficulties in testing are also discussed.

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2.6 THERMAL INTERFACES CONSISTING OF HIGHLY ORIENTED C-BASED STRUCTURES

Literature survey made by Bosch can be summarised as follows:

- Effective thermal conductivity of a vertically aligned CNT array is in the range of 70 – 80 W/mK [45]. This means a reduction of thermal interface resistance of 80 % compared to silver filled electrically conductive adhesives [46]. (see Figure 1)

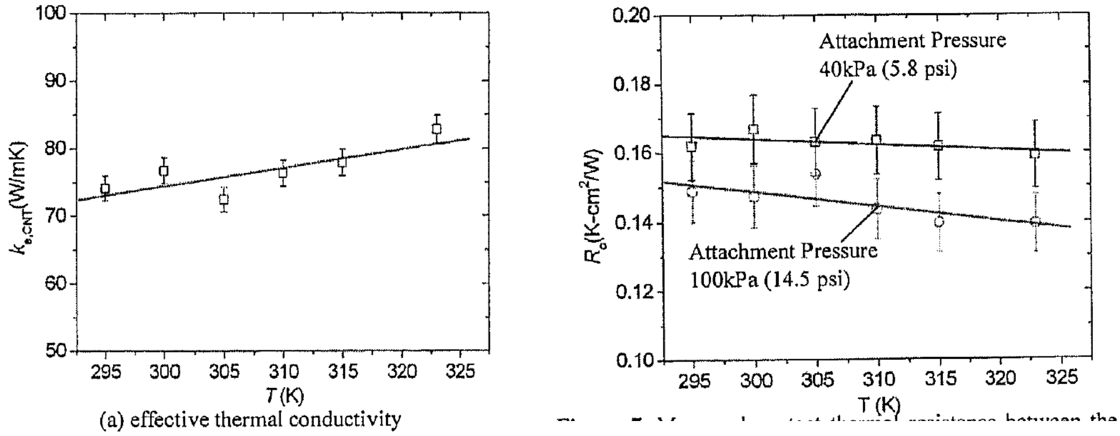

Figure 1 : Effective thermal conductivity (a) and thermal interface resistance (right) of a 13 µm thick CNT film grown on Si by PECVD (from [45])

- Thermal contact resistance between the CNT array and mating surfaces contributes significantly to the overall thermal resistance [48]. The use of electrically conductive adhesives reduces the thermal contact resistance significantly by establishment of an ohmic contact [49].

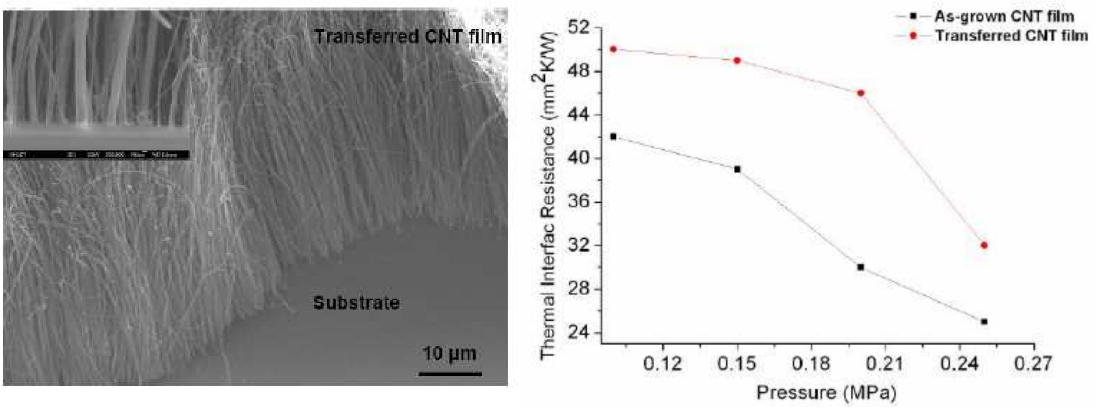

Figure 2 : SEM image of a transferred CNT film (left) and comparison of its thermal resistance before and after film transfer (right) (from [48])

- Simulations show that establishment of covalent bonds between CNT and mating surfaces have a great potential to reduce thermal contact resistance [50]. Furthermore, the length of CNT is most critical factor in bulk thermal conductivity of a CNT-polymer composite, i.e. to span the bond line by single tubes. Filler content and bending of CNT are no critical factors [51].

Patent survey can be summarised as follows:

- GeorgiaTech holds a patent on growing vertically aligned CNT arrays on silicon [52]. Transfer methods have been shown on conferences [49], but not filed.
- Intel holds a patent on aligning of CNT in polymer composites by means of highly oriented fillers (clay), or liquid crystal polymers by extrusion. Orientation of CNT between magnetic particles by external fields is described also [53].
- More patents on compatibilisation of C fibres with polymers can be found.
- A lot of process details are not yet patented nor filed.

Conclusions :

Thermal interface materials based on aligned C or CNT in a polymer matrix are promising candidates to provide competitive solutions for high power applications. Concepts for improvement of thermal contact resistance are missing and need further research. Reliability of these materials in automotive applications needs to be assessed also.

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3 THERMALLY CONDUCTIVE ADHESIVES AND COMPOSITES

The thermally conductive adhesives and composites are classified into three categories based on the type of filler.

3.1 CARBON NANOTUBES (CNTS)

CNTs including multi-wall (MW) and single-wall (SW) CNTs can exhibit extremely low percolation concentration threshold (<0.01wt%) in polymer matrices [1,2]. In fact, percolation thresholds were frequently reported below ~1wt% depending on the dispersion state of CNTs in the matrix [3]. Therefore, small CNT loadings (a few wt% or a few vol%) are usually used for CNT/polymer composites. The thermal conductivities of epoxy composites containing a few wt% CNTs were generally reported to be 0.25-0.6W/mK at ambient temperature [3-6]. The small increases in thermal conductivity in these composites are attributed to a large interfacial thermal resistance at the CNT/polymer interface. Currently, the thermal conductivities of CNT/polymer composites are much smaller than those of commercial Ag/epoxy adhesives.

The thermal conductivity of the CNT/polymer composites can be controlled by alignment of CNTs [7,8]. Although the aligned CNT/polymer composites exhibit anisotropic conductivity, high thermal conductivities can be obtained along the CNT alignment direction. For example, the thermal conductivity of an aligned CNT/poly-dimethly siloxane composite (CNT loading: ~2vol%) was reported to be 1.8-3.8W/mK at ambient temperature along the alignment direction [8].

3.2 CERAMICS

There are many reports concerning the thermal conductivity of polymer composites containing ceramic fillers such as BN, AlN, SiC and Al_2O_3 [9-16]. In these papers, the experimental data were often analyzed using FEM [16] and mixture rules including Maxwell-Euken, Bruggemann, Agari, Nielsen and Hatta-Taya models. The thermal conductivities of the composites with ceramic filler loadings below 40-50vol% are considered to be possible to analyze these models except the Maxwell-Euken model.

In addition, the concept of effective thermal management by maximizing the formation of conductive networks while minimizing the heat resistance along the heat-flow path is well recognized [17]. In order to achieve such composites, two kinds of strategies are currently proposed. One is the bimodal size distribution of fillers in order to obtain high packing density composites [17-20]. The other strategy is the improvement of adherence between the matrix and filler [20,21]. It is known that the interfacial thermal contact resistance between different constituent phases due to the phonon scattering can arise from the combination of a poor mechanical or chemical adherence at the interface and a thermal expansion mismatch. Therefore, the surface modification of filler using coupling agents is performed in order to enhance the interfacial thermal conductance.

3.3 AG AND OTHER METALS

Ag flakes and particles are commonly used as filler for electrically conductive adhesives. For the last decades, the material designs based on the bimodal concept using nanoparticles [22,23] has been studied in order to improve electrical conductivity of the adhesives. The contact resistance between fillers is also expected to be decreased in the bimodal adhesives because Ag nanoparticles are potentially sintered even at <200ºC [24]. However, the nano Ag filled conductive adhesives frequently showed higher electrical resistivity than the micrometer-sized Ag flakes filled ones [13]. The first success in the bimodal conductive adhesives using Ag nanoparticles was reported from Harima Chemical in 2001. The bimodal conductive adhesives developed by Harima Chemical exhibit low electrical resisitvities (~6 x 10^{-6} Ωcm) after curing at appropriate conditions. They had already commercialized the bimodal conductive adhesives (Hybrid silver paste) in Japan [25]. Recently, Wong et al. have also successfully developed the conductive adhesives using Ag nanoparticles [26].

They used a diacidic surfactant (carboxylic diacid) for the nanoparticles. Because the diacid molecules can accelerate the sintering of nanoparticles, low electrical resistvites (~5 x 10^{-6} Ωcm) were obtained after curing the adhesives.

Some papers reported thermal conductivities of the conductive adhesives containing micrometer-sized Ag fillers (flakes, spherical particles) [27,28]. The values of thermal conductivity are varied depending on the binder chemistry (binder type, curing condition) and Ag loading levels. In addition, the adhesives containing Ag flakes frequently exhibit anisotropic thermal conductivity. In the case of thin film specimens, the Ag flakes tend to align with the longer dimension parallel to the film surface. In the case of such specimens, the in-plane thermal conductivity (λ_{xy}) is higher than the through-plane thermal conductivity (λ_z). Furthermore, the bondline effective thermal conductivities were also measured using multilayer specimens (e.g., Si/adhesive/Si). The bondline effective thermal conductivities of the adhesives containing Ag fillers (30-60vol%) reach to 7-10 W/mK [27].

The thermal conductivities of the polymer composites containing other metallic fillers (such as Ni and Cu) were also reported [29,30]. Although the material cost would be reduced by using these fillers, the composites usually exhibit high electrical resistivities due to surface oxidation layer on filler particles. The thermal conductivities of the composites are limited to 2-4 W/mK (filler loading: 30-50vol%).

3.4 REFERENCES

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4 CARBON NANOTUBES AS FLIP CHIP INTERCONNECTS

4.1 INTRODUCTION

Along with the integrated circuit (IC) performance increasing, many technical challenges appear in the areas of current-carrying capacity, thermal management, I/O density, and thermal-mechanical reliability. Carbon nanotubes (CNTs) have drawn a lot of attentions due to the combination of their extraordinary structural, electrical, mechanical and thermal properties, and wide range of potential applications [1-13]. Many groups are now pursuing various approaches for using CNTs in microelectronics because of their high current carrying capacity, excellent thermal conductivity and low thermal expansion coefficient. In combination with conventional materials, it is likely that CNTs will be implemented as a hybrid solution in interconnect technologies. Much effort focus on using CNTs as on-chip interconnects to satisfy the future large scale integrated circuit requirements. Efforts to utilize CNTs as off-chip interconnects are also under intensive research in both academia and industry.

4.2 WHY SELECT CNTS

There is a major shift in first-level interconnect (chip to package or board) from wire-bonding to flip-chip. Despite flip-chip is more costly than wire-bonding, even in high volume, the switch to flip-chip interconnection is necessary to increase chip performance. Starting with C4 process from IBM, numerous alternative bumping methods have been successfully developed during the past decades including solder bump, indium bump, gold bump, copper bump, etc.[14] Most of current bumping technologies are facing challenges in fine pitch application because of high density and miniaturization requirement. The demand for a high population of smaller and smaller solder bumps have resulted in a significant increase in the current density, which makes electromigration the limiting factor in high density packages according to the International Technology of Roadmap for Semiconductors (ITRS) requirements. The enhanced current density and correspondingly upgraded operating temperatures are critical issues in reliability since these factors facilitate the effects of electromigration [15-17]. Therefore, it was realized that the solder bump is not able to fulfill the demands of high-speed and high-performance interconnects.

To overcome the above problems, different alternative solutions have been proposed, among which optical interconnects and carbon nanotubes are believed to be the most promising technologies. The optical interconnect has become an intense research area for over 15 years due to several advantages, such as reduced delay, no interference at interconnection crossings, no crosstalk between high-density signal lines, reduced power loss, etc. [18] Although optical fiber has been successfully used for long range communication, the use in off-chip and on-chip interconnects has been limited only in laboratories. The main difficulties are the yield of the modulators, the large area and power consumption of the optical components and driving circuits, generation of sufficient optical power, on-chip fabrication of the interconnect, and silicon optoelectronics circuit packaging, etc.[18] Other challenges include the fabrication of efficient room temperature silicon light emitters, temperature sensitivity of the light emitters and photodetectors, and bulk manufacturing at a competitive cost. Some good debates on optical interconnects can be found in references [18-22]. The references [23, 24] are two representative examples of recent demonstrations of optical off-chip interconnects.

CNTs exhibit a ballistic flow of electrons with electron mean-free paths of several micrometers, and are capable of conducting very large current densities (exceeding 10^9 A/cm^2, which should withstand a 1000 times higher current density than Copper) [8-10]. Furthermore, sufficient heat removal from the chip might be accomplished by CNTs due to their superb thermal conductivity, which exceeds that of diamond [13]. The CNTs are also believed to have larger lifetime compared to conventional interconnects. Compared to optical interconnects, integrating CNTs into CMOS technology is likely to be relatively easy. This section gives a short review of CNT-based off-chip interconnects.

4.3 CARBON NANOTUBES

Since their discovery in 1991, carbon nanotubes have received tremendous research interest [1]. The CNTs encompasses tubular nanostructures composed of graphitic carbon. There are two main types of carbon nanotubes [2, 3]: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). A SWCNT is a single layer graphene rolled with a diameter of 0.4 nm to a few nanometers and a length with over several millimeters, while MWCNTs, on the other hand, are concentric graphene tubes that may have diameters from a few to a hundred nanometers. Depending on its chirality, the SWCNTs can be either metallic or semiconductor. Due to the helical arrangement of carbon atoms in SWCNTs is random during the growth process, statistically 2/3 of the randomly produced SWCNTs are semiconducting and 1/3 of them are metallic [4]. For the application as interconnect materials, metallic SWCNTs are of great interest and show three main interesting electrical properties (e.g. [4-6]) including a scattering free electron transport, a mean free path of conduction electrons as large as several micrometers and an impressive current density exceeding to 109 A/cm2. A CNT is very close to a one-dimensional (1-D) system of electrons that's why it has so many unique electrical and thermal properties. A three-dimensional (3-D) metallic wire in which electrons can be backscattered by a series of small angle scatterings, and the mean free path is in the range of a few tens of nanometers [7]. Here any scattering gives rise to electrical resistance of metallic wire. Since electrons in carbon nanotubes can move in 1-D only, the phase space for scattering is very limited and electrons can be scattered only backward. Backscattering requires very strong collisions and is thus less likely to happen due to very small diameter and huge ratio of length to diameter of nanotubes. Compare to the 3-D metallic wire, 1-D CNTs have extremely low electrical resistance because of fewer possibilities to scatter. And the mean free path in high quality nanotubes is in the micrometer range. Therefore, one can achieve a long ballistic quantum conductor by increasing the diameter of the SWCNT, which is unattainable for conventional metallic wires. Moreover, due to the stacking of SWCNTs into bundles or rope reduces the disorder attributed to tube-environment coupling and the total capacitance, which make them promising materials for interconnects. MWCNTs can be considered as parallel concentric SWCNTs. Therefore, each grapheme shell may present electrical properties similar to an isolated SWCNT with the same helical structure. Although most electrical transport only make contact to the outermost shell of MWCNTs [8, 9], it is highly desirable for interconnect applications that electrical contacts can be made to each grapheme shell to form a parallel ballistic quantum conductor [10].

As a result of the carbon–carbon sp^2 bonding, the carbon nanotubes have high stiffness and axial strength. Nanotubes are the stiffest known fiber, with a measured Young's modulus of 1.4 TPa and a tensile strength of 150 GPa [11]. They also have an expected elongation to failure of 20-30%, which combined with the stiffness [12]. It is well known that both graphite and diamond exhibit extraordinary thermal conductivity and diamond is the best thermal conductor. CNTs have now been shown to have a thermal conductivity at least twice that of diamond and have the unique property of feeling cold to the touch. The specific heat and thermal conductivity of carbon nanotube systems are determined primarily by phonons. The thermal expansion property of CNTs is another factor making them attractive for interconnect materials. This property is very important to define the reliability of interconnects under thermal cycling [13].

There are mainly three methods to synthesize CNTs: arc-discharge, laser ablation and chemical vapor deposition (CVD). The first CNTs were produced by accident from the arc-discharge technique by Iijima who was using the method to produce fullerenes in 1991 [1]. Arc-discharge is the easiest and most common method of producing CNTs. This technique involves the growth of CNTs on carbon electrodes during the direct current arc-discharge evaporation of carbon in the presence of an inert gas such as helium or argon. Laser ablation is another method to synthesize the CNTs. Guo et al. were the first to synthesize CNTs by this method [25]. More specifically, SWCNTs were synthesized by the laser vaporization of a mixture of carbon and transition metals located on a target. Arc-discharge and laser ablation can produce CNT materials with the highest crystalline quality, but both of them have a drawback of remaining many unwanted impurities in the bulk materials, which are quite cumbersome to purify. Moreover, it is quite difficult to scale these growth methods for mass production. The recently developed CVD method involves the decomposition of a hydrocarbon in the presence of a catalyst and takes place at much lower temperatures. Catalytic growth of nanotubes by the CVD method was first used by Yacaman et al. [26]. Typical hydrocarbons are ethylene or acetylene, which are decomposed in a tube reactor at temperatures ranging from 600 to 900 °C. CNTs are grown by selective catalytic CVD, which means that CNTs only grow where there is a catalyst, typically Fe, Co, or Ni [27]. It can be found that all of them have advantages and disadvantages. Since large-scale production of CNTs is becoming the most important factor and the defining issue has become the selection of the best method for commercial applications, most industries and institutes today are opting for the CVD technique. There are two main classes of CVD method, namely, thermal and plasma enhanced. Both of them share many similarities. The major difference is in the type of the heat source that is employed during the growth. Thermal CVD uses conventional heat sources such as a tube furnace to heat the walls of a process tube [28], while plasma enhanced CVD applies plasma generating source or in combination with conventional heat sources [29].

4.4 CNTS AS FLIP CHIP INTERCONNECTS

Metallic CNTs are a promising candidate for applications as interconnects. As we have mentioned above, the CNTs exhibit extraordinary characteristics such as high current carrying capacity, low resistence and high thermal conductivity. Taking full advantage of these preperties, the CNTs also can used as bumping interconnects. Due to the lack of control on chirality, any bundle of CNTs consists of metallic as well as semi-conducting nanotubes and the semi-conducting CNTs do not contribute to current conduction in an interconnect. The quantum resistance is 6.45 kΩ which is too high for practical interconnects. Because the SWCNT bundles or rope consist of several individual SWCNTs and they can conduct current in parallel, they can solve the problem of high resistance of an isolated CNT and are the desirable materials for interconnects. Moreover, theoretical studies show that carbon nanotubes, if packed closely enough together, should be an ideal electrical conductor. Therefore, the tightly packed CNT bundles are efficient conductors and could be the primary interconnects and even hasten the transition to next-generation 3-D stacked chips.

Fujitsu laboratories pioneered the application of CNTs as flip chip interconnects [30, 31]. The CNT bumps demonstrated in Fujitsu’s papers are still relatively large. And some technical details are not clearly described in these two papers. Using CNTs as on-chip interconnects, mainly as fillers of vias, is also under development at Fujitsu. A few representative papers are references [32-34]. Other institutions involved in this field include Georgia Institute of Technology, Hong Kong University of Science and Technology, and Rensselaer Polytechnic Institute, etc.

4.5 TRANSFER OF CNTS

The CVD technique suffers from some disadvantages. One of the main challenges of fabricating CNTs is the high growth temperature, which is not compatible with some temperature-sensitive processes and materials, thus preventing the utilization of CNTs in these cases. For instance, putting ICs under this temperature may destroy the active devices inside the chips due to the process of ICs is typically below 400-500 °C. Another one is the poor adhesion between CNTs and substrates, which will result in long term reliability issues and high contact resistance. To overcome these problems, a possible solution is to transfer CNTs onto the target substance at low temperature after the growth process. Huang et al. have reported contact transfer of well-aligned CNT films by using a transimission electron microscopy grid in the transfer process to create patterns of CNT films [35]. Similarly, Dai et al. have developed another simple but very effective and versatile dry contact transfer tequnique by using a Scotch tape for controlled preparation of 3-D vertically aligned CNT micropatterns [36]. This work starts with adhering a TEM grid onto Scotch tape as a mask, followed by sputter coating with silver through the mask. Then, the silver-patterned Scotch tape is subjected to plasma treatment. After removal of TEM grid, the Scotch tape is pressed on the as-synthesized vertically aligned CNT film on a quartz plate. Then the Scotch tape is peeled off from the quartz substrate. Finally, nanotubes underneath the silver-free regions are selectively transferred onto Scotch tape. The silver-free regions as a positive image of the TEM grid whereas those covered by siliver-patterned areas remain on the quartz substrate as a negative pattern. However, the utilization of the grid and Scotch tape in these two processes limits CNTs application. Furthermore, L. B. Zhu et al. also proposed a simple but efficient process to achieve simultaneous CNT growth and opening of the CNT ends [37]. By using unpatterned or patterned metal alloys, CNTs can be transfered to conductive substrates, but the transfer requires relatively high temperature (250-300 °C) and long time (2 h) [38]. After that, A. Kumar et al. reported another transfer CNTs by using sliver paste, in which the annealing is carried out at even higher temperature (530 °C) [39]. Recently, a lift-off technique to transfer aligned CNT films was reported but the adhesion between CNT film and the substrate is weak and no patterning can be implemented in the process [40]. Using conductive adhesives to transfer a whole CNT film at low temperature has also recently been reported [41], but no patterning technique was applied.

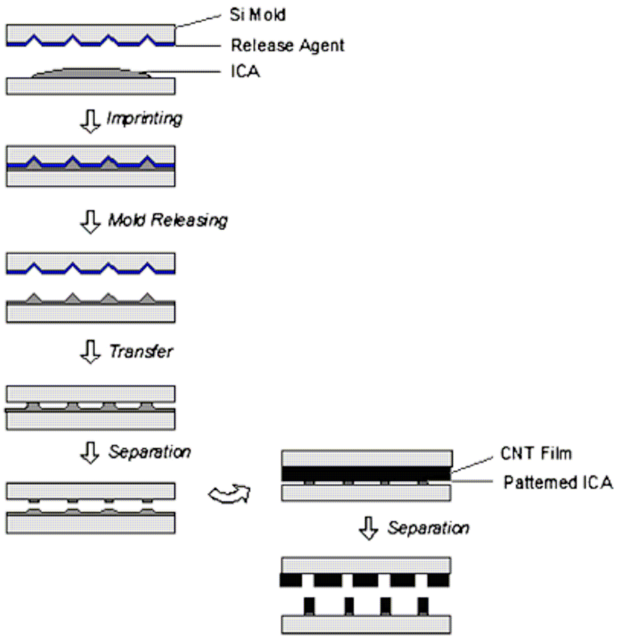

Figure 3 : Schematic diagram of the experimental process.
The ICA is patterned by an imprinting and heat transfer process and then utilized to transfer and form CNT bundles from a CNT film.

Vertically aligned CNTs are often grown on silicon in the form of square arrays of different sizes, heights and pitches. In our recently work, attempts to use thermal compression and anisotropic conductive adhesive to bond chips carrying CNTs bumps with ceramic substrates are executed [42]. Mechanical testing is performed afterward to determine the strength of the bonding interfaces. The strength of the bonding by thermal compression is very weak. The bonding by anisotropic conductive adhesive is much stronger, indicating a possible approach to bond chips carrying carbon nanotube bumps. Followed by this, we have developed an efficient, scalable, and low-cost process to transfer and form CNT bundles at a low temperature using patterned isotropic conductive adhesive (ICA) [43]. The patterning of ICA is performed by an imprinting and heat transfer process, which can be applied for a variety of interconnect purposes. The process was illustrated in Figure 3, containing two main phases: patterning of the ICA and transfer of CNTs. A drop of the ICA was placed in the center of a piece of silicon and then imprinted by the mold. Before the imprinting process, the silicon mold is spin coated with a thin layer of release agent, which prevents the conductive adhesive from sticking to the mold. The imprinting is carried out by a flip-chip bonder. After the printing, the mold is removed and the ICA is formed as uniform pyramid-like structures. Subsequently, a second silicon substrate is placed close to the original substrate and is previously sputtered with a thin titanium/gold layer which assists the electrical test in the latter stage. The two substrates are kept parallel and the gap between the two substrates is fixed at 20 μm during the transfer process. The silicon chips carrying CNT films are then used in the CNT transfer process. Transfer of CNTs and formation of CNT patterns are achieved simultaneously. Figure 4 shows the scanning electron microscopy (SEM) images of transferred and patterned CNT bundles as well as the cavities left in the original film. Arrays of fine pitch CNT bundles for bumping interconnects are produced. The current-voltage response is approximately linear in the measurement range and the resistance of this structure is around 100 Ω, which is quite low compared to the resistance derived before. *I-V* measurements verify that good electrical contact between CNTs and ICA was established in the transfer process.

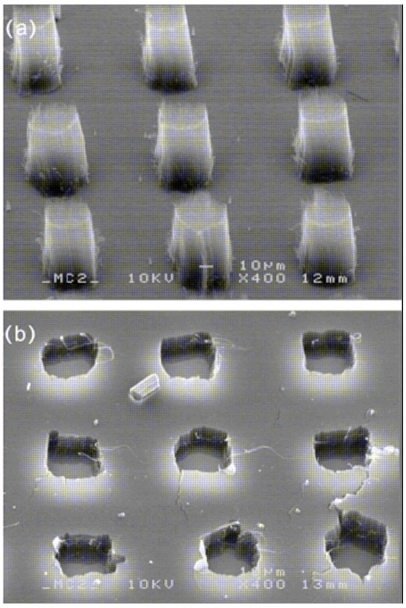

Figure 4 : (a) SEM image of an array of transferred CNT bundles with ICA underneath. (b) Cavities are left on the original CNT film.

4.6 THE CHALLENGES TO CNTS FABRICATION

Although the synthesis of aligned CNT bundles have obtained some advances, the fabrication of CNT interconnects poses several challenges because of the need for low thermal-budget, dense metallic SWCNT bundles [44-46]. The critical challenge facing the development of most CNTs based as interconnects is the reliable CNTs-metal contacts. As observed by Th. Hunger et al., making a reliable contact to a CNT is very challenging, and the resistance arising from these imperfect contacts is often so high that it masks the observation of intrinsic transport properties [47]. Due to the presence of imperfect metal-nanotube contacts which give rise to an additional contact resistance, the observed dc. resistance of a CNT is much higher than the resistance derived theoretical value in practice. The observed resistance for CNTs has typically been in the range of 100 kΩ [47, 48], although in a few cases the lowest observed resistance has been seen to approach the theoretical limit of 7 kΩ [48]. So far, the feasibility of using bundles of metallic MWNTs as vertical wiring materials has already been proved [25]. But most reports suggested that one of the most important issues regarding CNT vias was a need to reduce their resistance. M. Nihei et al. have succeeded in lowering the resistance of MWNT bundles by using parallel channel conduction of each tube’s inner shells. The corresponding resistance of about 0.7 kΩ per MWNT indicates that most of the inner shells contribute to carrier conduction as an additional channel [26]. The total resistance of the CNT bundles is comparable with conventional interconnects. The second challenge is the annealing of defects in nanomaterial building blocks. As has been indicated, the physical properties of CNTs are strongly dependent on structural defects and impurities in the graphite sheets comprising the tubes. A plethora of CNT sub types that show remarkably different physical characteristics will be obtained depending on the growth technique employed. Although CVD technique has shown many promising benefits, the as-grow material in some cases has many structural defects. Therefore, how to improve the growth technique and get the pure nanostructure is the issue many groups pursued. It is well known that CNTs appear as "noodles" as deposited on substrates and inside trenches, which is undesirable and the third challenge facing CNTs fabrication. The anticipated ballistic transport is unlikely to happen because of the entangled nanotubes. Although the reported fill factor is low and can be improved in the future, planarization by chemical mechanical polishing (CMP) is likely to unravel the noodles. Moreover, the problems associated with etching of high aspect ratio vias and seeding the bottom of a deep trench with a catalyst for CNT growth also appear in the fabrication of CNTs. This sidewall catalyst deposition can cause undesirable sidewall CNT growth, which results in the vias being filled but no electrical contacts to the bottom. Recently, J. Li, et al. provided an alternative bottom-up process in which MWCNTs are first grown (using HF-CVD) at prespecified locations, then gap-filled with oxide and finally planarized [49]. This bottom-up approach eliminates the etching step, already provides an aspect ratio of 20 or more uniform diameter interconnects, and eliminates void-related problems. However, the quality of CNTs grown using this technique is still low and so is electrical conductivity.

Finally, although MWCNTs are metallic in nature, they are less favourable for interconnects because they typically exhibit ballistic conductance over very short lengths (few nanometers) as compared to SWCNTs which have typical mean free paths of several micrometers [50]. The fertility of the catalyst particles for SWCNT growth is very low, therefore, it still difficult to grow bundles of SWCNTs for interconnects until recently. Although recent progress has been made in growing bundles of SWCNTs by addition of water or oxygen to increase the fertility of the growth catalyst [51, 52], this approach has not yet been applied to the fabrication of interconnects.

4.7 CONCLUSION

We have reviewed the unique material properties and synthesis of CNTs and described the current status in developing CNTs as potential interconnects, especially bumping interconnects. Many reports focused on the aligned CNTs synthesis and have obtained many advances on it. However, there still some challenges facing the fabrication of CNTs. Although CNTs show many promising potentials as interconnects, but there's still a lot of work to do before this technology can be integrated into industrial application.

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5 TIMS WITH MICROCHANNEL SURFACE MODIFICATION (IBM CONTRIBUTION)

Viscous particle filled materials are preferred in industry to form thermal and electrical interfaces due to their low cost and ease of application compared to rare metal alloys which have much higher material costs and require surface preparation steps. In order to get the highest conductivity from particle filled materials a relatively high volumetric loading (50-80% particles) is required. As the loading is increased the effective conductivity increases however at a cost of increased viscosity and particle interactions such as stacking that can prevent the formation of thin bondlines. The use of hierarchical nested surface channels (HNC) has been shown[1] to reduce interface resistance due to thinner bondlines (see Figure 5) and shown to reduce the required squeeze loads (see Figure 6). The surface channels ability to easily evacuate material from the interface with low assembly loads help maintain thin bondlines at the center of the interface for large area and thin substrate applications that are mounted with only peripheral loads applied (i.e. bolted).

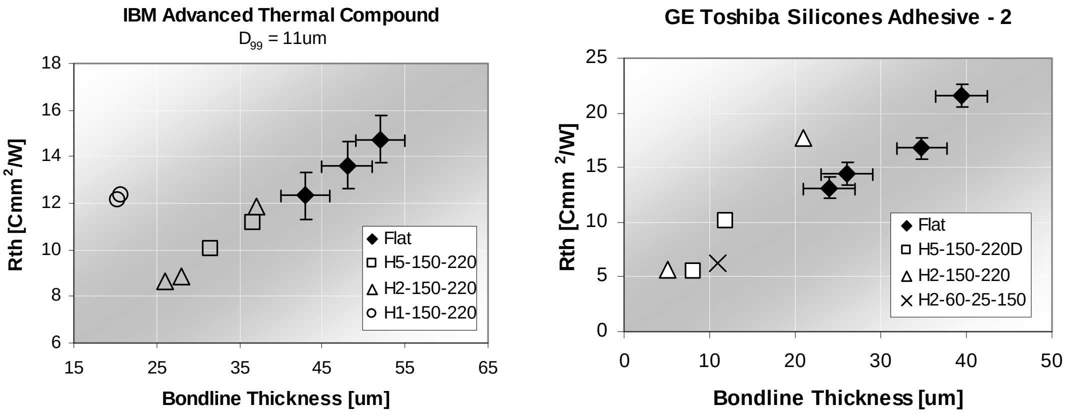

Figure 5 : Thermal resistance benefit from various HNC interfaces compared with a flat surface. (a) IBM ATC D_{99} = 11 µm, (b) GE Toshiba Silicones adhesive-2. Bondline conditions: 5 bar assembly load, 19.7-mm-square chip, 200 W, temperature ~30℃.

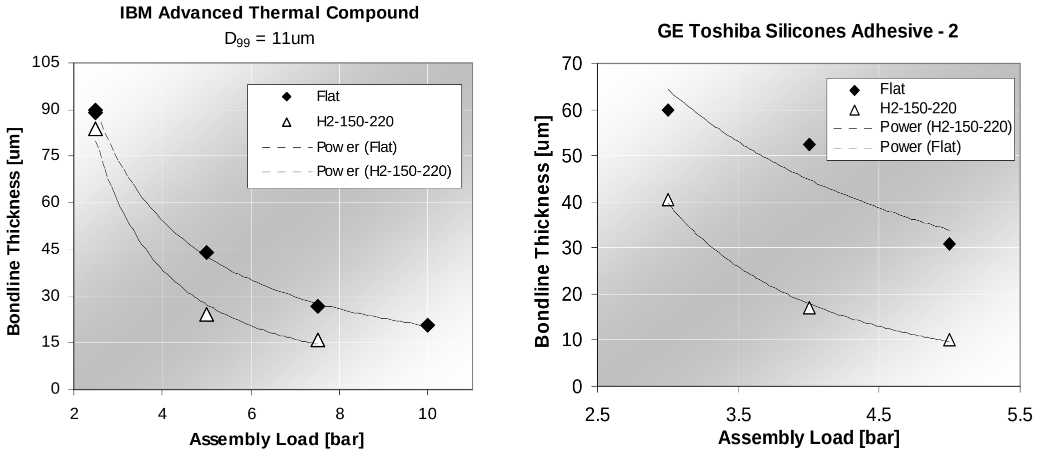

Figure 6 : Reduced assembly pressure associated with HNC for two thermal interface materials.

Because the surface channels alter the flow pattern of viscous material during assembly they also prevent the non-uniformities that typically develop during bondline assembly such as particle stacking formations between chip corners. The individual HNC cells actually create periodic arrays of particle stacks (see Figure 7) typically with a thinner bondline due to the delay in particle interactions until later in the squeeze process. The small scale stacking pattern within each HNC cell is formed due to the bifurcation of the flow to each edge of the cell. Because the the orientation and concentration of suspended particles is highly dependent on localized shear flow, the ability of the channels to redirect flows as desired may allow the exploitation of anisotropic properties in materials with high aspect ratio micro and nanoparticles. Oriented or optimized particle stacks could produce arrays of micro thermal and electrical vias that significantly improve performance.

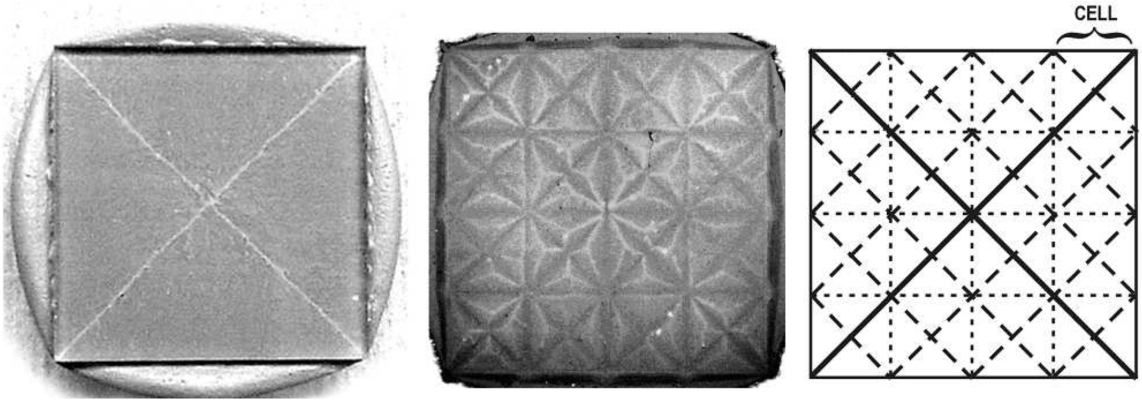

Figure 7 : Particle stacking associated with flat interfaces (left) and HNC (middle) with a standard nested channel layout shown on right.

The performance gain with the surface channel technology is highly dependent on the interface material used as well as the stiffness of the substrates/package and the support boundary conditions (periphery, central or uniform supported). Given the high sensitivity to the interface material it is important to study and develop particle and matrix systems that exploit the reduced assembly pressure and optimized flow pattern characteristics of the HNC technology. The effects of uni-modal, bi-modal and tri-modal particle mixtures would be a basic starting point to better understand the microscale structure of the particle stacks.

5.1 REFERENCE

[1] R. Linderman, T. Brunschwiler, U. Kloter, B. Michel, “Hierarchically nested surface channels for reduced particle stacking and low thermal resistance interfaces”, SemiTherm Symposium, San Jose, CA, March 20-23, 2007

6 CONCLUSION

This report has provided a refined analysis of existing TIM technologies for **WP2 (Development of materials)** T0+3 -> T0+27.

The objectives of WP2 are :

- To find out desirable nano-TIM compositions where nano-fillers and matrix may well be incorporated, and to optimize dispersing technologies to generate minimum thermal and electrical barriers between nano-fillers and matrix and to achieve a maximum thermal and electrical conductivity;
- To synthesize new nano-structured materials such as nanoparticles, nanotubes, nanofibrils packed nanoparticles, and nanograss for nano-TIM and electrical interconnection applications;
- To supply other work-packages with nano-TIM for characterization, modelling, simulation and demonstration and to optimize nano-TIM according to their feedbacks;
- To develop high performance nano-TIM which meets the requirements as specified in Work-package 1.
- To set-up a pilot line for manufacturing nano-TIM

WP2 will develop and manufacture high performance nano-TIM which meets the requirements as specified in WP1.