NANO-ENGINEERED CARBON NANOFIBER-COPPER COMPOSITE THERMAL INTERFACE MATERIAL FOR EFFICIENT HEAT CONDUCTION

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Abstract

Efforts in integrated circuit (IC) packaging technologies have recently been focused on management of increasing heat density associated with high frequency and high density circuit designs. While current flip-chip package designs can accommodate relatively high amounts of heat density, new materials need to be developed to manage thermal effects of next-generation integrated circuits. Carbon nanofibers (CNF) have been shown to significantly enhance thermal conduction in the axial direction and thus can be considered to be a candidate for future thermal interface materials by facilitating efficient interfacial thermal transport.

Introduction

Progress in the scaling of integrated circuits has resulted in an alarming rise in power dissipation in high-density, high-frequency silicon based microprocessors [1]. The need for addressing this problem is imperative for maintaining reliability standards for next-generation IC packaging technology [2,3]. The knowledge gained from addressing issues in microprocessor packaging can also be generalized to most devices that exhibit high power dissipation. The space program at NASA is also in need of thermal interface materials to draw heat away from hot spots on critical electronic components. One of the current issues with cooling systems for space vessels is the degradation of such systems over time. Liquid-cooled systems and those with moving parts do not fit this requirement due to their lack of stability and the need for constant servicing. Carbon nanofiber composites are a strong candidate material to provide thermal solutions for space missions.

Thermal characteristics of carbon nanotubes (CNT) and carbon nanofibers (CNF) have been measured [4-7] revealing their unique thermal conductivity characteristics along the nanotube axis. For a discrete multiwall carbon nanotube (MWNT), thermal conductivity has been measured surpassing 3000 Wm⁻¹K⁻¹ in the axial direction [4]. Other studies have reported values for discrete MWNTs as small as 15 (Wm⁻¹K⁻¹) [5] and 27 (Wm⁻¹K⁻¹) [6]. The wide variation can be attributed to the inherently defective nature of some carbon nanostructures grown by the chemical vapor deposition (CVD) process [8]. Despite this variability in intrinsic conductivity, CNFs may still be capable of improving heat conduction at interfaces by increasing contact area. In this work, we combine CNF arrays with copper by gap-filling copper between the nanofibers with an electrochemical deposition (ECD) process. The
resulting composite improves lateral heat spreading capabilities of the composite and serves as a mechanical anchor for the nanofibers to the substrate.

Through the use of DC-biased plasma-enhanced chemical vapor deposition (PECVD) [8], we fabricate vertically aligned, freestanding CNF arrays on silicon wafers of ~500μm thickness. Copper electrodeposition, a common process used for gap-filling high aspect ratio trenches, is used for the creation of a CNF-Cu composite array. The data presented here demonstrates the mechanical strength and efficient interfacial heat conduction of CNF-Cu composite arrays suitable for this next-generation thermal interface material.

**Carbon Nanofiber (CNF) Array Growth**

CNF arrays were grown using the procedure and reactor conditions detailed in ref. 8. A layer of titanium (300Å) was used as both an adhesion layer for a thin layer of nickel catalyst used for the CNF array growth and as a seed layer for the subsequent copper electrodeposition. From SEM images of the as-grown samples (Figure 1), we estimate the height of the nanofibers as approximately 7.5μm. This information allows us to determine a target for how much copper should be deposited. The nanofiber heights can be controlled from 1μm to 30μm by tuning the PECVD conditions. The CNF array has a random lateral distribution with an approximate average spacing of 200nm to 300nm. Cross-sectional transmission electron microscopy (TEM) reveals the bamboo-like structure of carbon nanofibers grown in the PECVD process (figure 2). The graphitic sheets crossing over the center axis of the CNF in figure 2(a) are characteristic of the bamboo-like morphology. These defects are inherent in vertically-aligned CNFs grown using the PECVD method [8,9]. Figure 2(b) shows a schematic of the bamboo-like structures, exhibiting approximately a 5-10° cone angle deduced from high-resolution TEM of the sidewall of the CNFs. It is as yet uncertain how much this tube structure affects the heat transport through the tube in the axial direction.

**Figure 1.** Carbon nanofiber array grown by plasma-enhanced chemical vapor deposition.
Composite Fabrication Using Copper Electrochemical Deposition (ECD)

Due to stringent processing and technology requirements for copper interconnect structures in ICs [2], many processes have had the need to fabricate high aspect ratio copper interconnect structures. One such approach is the use of copper electrodeposition with a combination of additives in the electrolyte bath to promote "bottom-up" growth of narrow copper features [10]. The deposition in this work is performed in a three electrode setup with the forest-like CNF array (with a cross-sectional area of 1-2 cm$^2$) as the working electrode (WE), a Saturated Calomel Electrode (SCE) as the reference electrode, and a one square inch platinum foil as the counter electrode (CE), set in parallel with the CNF sample. The bath consists of 100 ppm chloride ions (Cl$^-$), 400 ppm polyethylene glycol (PEG, molecular weight of 8000), 10 ppm bis(2-sulfopropyl) disulfide (SPS), 10 ppm Janus Green B (JGB), 0.6 mol/L copper sulfate (CuSO$_4$•5H$_2$O), and 1.85 mol/L sulfuric acid (H$_2$SO$_4$). In the presence of Cl$^-$, PEG molecules adsorb on the top of the high aspect ratio nanostucture and inhibit the Cu electrodeposition from sealing off the gaps between nanofibers. SPS and JGB are used to accelerate the electrodeposition rate within the trench [10]. The deposition quality is a function of a variety of parameters such as electropotential, time, the selection of seed layer metal, and length distribution and density of the nanofiber array. The potential/current and time determine copper deposition rate and amount of copper deposited, respectively. The approximate deposition rate for the copper ECD process used here is 430 nm/min. From the amperometry data (current versus deposition time), we can determine the amount of charge deposited on the sample, thus determining the approximate thickness of copper deposited using equation (1).

\[
I_{Cu} = \frac{Q \cdot M_{Cu}}{2 \cdot F \cdot A \cdot \rho_{Cu}}
\]

$Q$ is the amount of charge deposited in the ECD process, obtained by integrating current with respect to time, $M_{Cu}$ is the molecular weight of copper, $A$ is the area of the sample, $F$ is Faraday’s constant, and $\rho_{Cu}$ is the density of copper.

While the resulting CNF-Cu composite film is controlled by altering deposition time, it provides a very rough copper surface and, in some cases, leaves copper at the ends of the nanofibers. Therefore, an electrochemical etch has been introduced to smooth the copper surface [11]. This is done in an 85% ortho-phosphoric acid solution using the same three-
electrode setup at a potential of 1.5V (vs. SCE). A 45 second etch resulted in the structure seen in figure 3.

**Figure 3.** a) Cross-sectional and b) 45° angle view of CNF-Cu composite after 45 second copper etch in 85% ortho-phosphoric acid solution.

**Thermal Contact Resistance Characterization**

An apparatus consisting of two copper blocks, with four resistive cartridge heaters embedded in the upper block and a cooling bath circulating to the lower block, was used to measure the thermal resistance of the CNF-Cu composite [12] (figure 4). The apparatus is designed to accommodate a 1” x 1” square area, corresponding to the dimension of the heated block. The thermal resistance of the sample can be calculated at a variety of powers and pressures using the following relationship:

\[
R = \frac{A(T_B - T_C)}{Q - C_L(T_B - T_{amb})}
\]

where \( Q \) is the total power, \( A \) is the sample area, and \( T_B, T_C, \) and \( T_{amb} \) represent the temperature of the upper block, the chilled lower block (20°C), and the ambient environment, respectively. \( C_L \) is a heat transfer coefficient used to estimate the heat loss to the ambient in this measurement configuration and is determined by placing a thick insulator between the two blocks and measuring the steady state \( \Delta T \) at a variety of constant powers, yielding \( C_L = 0.0939 \) W/K.

**Figure 4.** Apparatus used for thermal resistance measurement and equivalent thermal resistance model. \( T_B \) is the temperature of the block, measured using an embedded thermocouple.
As can be seen in the equivalent resistance model (figure 4), the measurement encompasses resistance components of the entire assembly, including the upper copper block resistance, CNF-Cu composite interface resistance, intrinsic silicon resistance, and the Microfaze A6 (AOS Thermal Compounds, LLC) resistance. Microfaze A6 is used to lower the thermal resistance on the backside of the silicon wafer. The particular interface we are interested in is the upper block to CNF-Cu composite interface. The characterization of this film alone is accomplished through determination of the copper block thermal resistance and two control measurements involving the bare silicon interface and Microfaze A6. $R_{Cu-block}$ is calculated assuming a linear variation of thermal resistance inside the block, from the thermocouple embedded 1.3 inches from the surface to the actual block interface. Using this assumption, we determine this value to be 0.83 cm$^2K/W$ for a one square-inch area based on bulk copper properties. For smaller sample sizes, the area is normalized to calculate the Cu-block resistance value. The control measurements are used to account for the resistance of the silicon, copper block, and Microfaze A6, allowing us to de-embed these contributions to determine resistance values of the CNF-Cu composite. To summarize, we can determine the interfacial contact resistance of the CNF-Cu composite interface when contacting the copper block by equation (3).

$$R_{CNT-Cu}(interface) = R_{total} - R_{Cu-block} - R_{Si} - R_{Microfaze}$$

$R_{Si}$ is the intrinsic resistance of the silicon. For the 500μm thick silicon wafer considered here, the calculated value of thermal resistance, based on the bulk thermal conductivity value of silicon, is 0.034 cm$^2K/W$, which is more than ten times below the final measured values of the CNF-Cu composite interface and thus can be neglected in this case. Two control measurements are used to determine $R_{Microfaze}$. The first measurement involves measuring the thermal resistance of a bare piece of silicon with Microfaze A6 on the backside of the wafer. This number gives $R_{control,1} = R_{Cu-block} + R_{block-Si} + R_{Microfaze} + R_{Si}$ where $R_{block-Si}$ is the interfacial resistance between the copper block and silicon wafer. The second control measurement involves characterizing a double-sided polished piece of silicon wafer, giving us $R_{control,2} = 2R_{block-Si} + R_{Si} + R_{Cu-block}$. By using the two-step control measurement, we can effectively account for the power and pressure variation of the material under test.

Figure 5 shows thermal resistance measured with respect to heat flux for a CNF-Cu composite film before and after correcting for the power dependence of the Microfaze A6. Constant thermal resistance values obtained for the nanofiber composite film at different heat fluxes demonstrate the validity of the control sample correction scheme. The Microfaze A6, however, shows a decrease in thermal resistance with increasing heat flux. The material mobility in the Microfaze A6 works to minimize thermal contact resistance under increasing heat flux by microscopically changing to fill voids in the thin polymer layer. The CNF-Cu composite, on the other hand, undergoes no change in contact area with added heat flux as the nanofibers are anchored to the substrate. Figure 6 shows thermal resistance measured for a single silicon interface and the CNF-Cu composite film interface at different pressures. In this case, the resistance decreased with increasing pressure, which is consistent behavior for most thermal interface materials. It also shows that the CNF-Cu composite provides a better contact at increased pressure. Also note that the bare copper film shows a higher thermal resistance at all pressures when compared to both silicon and the nanofiber composite. This is likely due to the interface roughness of the materials rather than their intrinsic thermal conductivity. Figure 6 illustrates the clear advantage of the CNF-Cu composite in improving thermal contact resistance, thereby enhancing interfacial heat conduction.
Figure 5. Thermal resistance versus heat flux for CNF-Cu composite film at 6.8 psi clamping pressure. The upper curve (crosses) shows the thermal contact resistance decreasing at increasing heat flux, while the lower curve (circles) shows the composite sample to be relatively independent of heat flux. The middle curve (triangles) shows the thermal resistance of an as-grown CNF array.

Figure 6. Thermal contact resistance versus pressure for CNF-Cu composite film at input power of 27.2 W. The upper curve (triangles) shows the interface thermal resistance of a bare copper film and copper block. The center curve (squares) shows the measurement result considering the single silicon interface with the copper block. The lower curve (diamonds) represents the interfacial resistance of the composite film with the copper block. The solid lines represent the best-fit data trends.

Comment [BAC1]: I have not seen the CNT-array data before. What did the sample look like? Any justification for an increasing resistance with heat flux?
A good point of comparison for the CNF-Cu composite film would be an as-grown CNF array exhibiting roughly the same length and diameter distribution. Such a structure can demonstrate the usefulness of copper gap-filling in the array structure. Indeed, as shown by the middle curve (circles) in figure 5, the CNF array shows a higher thermal resistance when compared to the CNF-Cu composite. The mechanism for such a difference in contact resistance can be explained by examining the microstructure of CNFs. The disordered nature of the nanofibers exhibiting graphitic crossover points throughout along the entire fiber has been shown to demonstrate good electrochemical properties on active sites located on nanofiber sidewalls [14]. Lateral heat conduction in the composite may also be enhanced by the active sites on each nanofiber.

**Conclusion**

In this work we have demonstrated the efficient thermal contact conductance properties of CNF-Cu composite materials. The composite material considered here has been tested at a variety of powers and pressures, yielding reasonable trends indicating the viability of their use as a thermal interface material in both IC packaging and equipment cooling applications. Values of thermal resistance as low as 0.25 cm²K/W have been obtained with the contact measurement technique employed here for pressures approaching 60 psi. Copper gap-filling between nanofibers using electrochemical techniques is introduced as a means for providing mechanical stability as well as lateral heat spreading capabilities to the system. Further optimization of CNF growth, copper gap-filling, and measurement methodology will be needed to improve on the promising results obtained here as we work towards implementation of this novel material into IC packaging process flows.

**References**


