Characterization of vertically oriented carbon nanotube arrays as high-temperature thermal interface materials

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Abstract

Carbon nanotube arrays hold much potential for high-temperature thermal interface applications that require thermal stability and mechanical compliance. A 1D reference bar test rig designed for measurements at and substantially above room temperature is used to perform thermal cycling tests on CNT arrays and to measure their thermal interface resistance at temperatures up to 700°C. The CNT arrays are synthesized and tested with both thermomechanically matched (Cu-Cu) and mismatched (alumina-Cu) interfaces to examine their mechanical compliance. For both cases, a moderate decrease in thermal interface resistance (TIR) occurs from room temperature to 700°C. The results reveal good cyclic stability of CNT arrays in both cases, confirming their ability to accommodate large thermomechanical mismatch. Post-mortem analysis indicates that CNT free ends conform to the opposing Cu surface. In the Cu-Cu interface, only compressive deformation of the CNT arrays is observed. In the alumina-Cu interface, more complex thermomechanical deformation occurs that is hypothesized to be a combined effect of compressive loading and shear stress.

Keywords: carbon nanotube, thermal interface material, high temperature, thermomechanical stress

Introduction

Thermal management issues have increasingly limited the development of electronic devices [1, 2]. When heat generated in devices is not rejected to heat sinks efficiently, high temperatures can cause significant performance degradation or even permanent damage. Naturally, a low thermal resistance is desired between the heat-dissipating device and its heat sink. In practice, a significant fraction of this thermal resistance comes from various material interfaces [3]. As a result, new thermal interface materials (TIMs) that can reduce interface thermal resistance when applied between two mating surfaces have been actively studied and developed in recent years. Conventional TIMs such as thermal greases, metal foils, graphite, and phase change materials have been improved and optimized [4], while at the same time nanostructured carbon-based

materials, especially carbon nanotubes (CNTs), have become an increasingly attractive option [5-8]. Many traditional TIM materials are limited to operation near room temperature, and very little prior work exists on CNT TIMs at elevated temperatures. The present study seeks to provide performance characteristics of the latter in terms of thermal resistance/conductance and durability.

Individual carbon nanotubes have been measured with thermal conductivities at room temperature of 1000-3500 W/mK [9, 10], although their thermal behavior in aggregate and composites can be much poorer [1, 3, 11]. Furthermore, vertically oriented CNT arrays have very low modulus in lateral directions and low compressive modulus in the vertical direction [12-14]. This excellent mechanical compliance is an ideal property for thermal interface applications, as CNTs can readily conform to asperities on the mating surfaces to increase real contact area.

Most microelectronic devices operate near room temperature ($<150^{\circ}\text{C}$) in atmospheric conditions. However, many emerging extreme-condition applications have created demand for a more robust interface solution. Thermoelectric generation (TEG) is being used increasingly with higher temperature heat sources in order to obtain better efficiency and more power output [15, 16]. For example, recent research programs aim to harvest the waste energy in automobile exhaust gas ($>600^{\circ}\text{C}$) using TEG [17-19]. The actual temperature at the hot-side junction of the thermoelectric device is often much lower than that of the heat source, mainly because of the high thermal resistance of various interfaces between them, and the high-temperature environment dictates that traditional organic-material TIMs cannot be used.

Direct bonding (e.g., brazing, welding, diffusion bonding) often results in low thermal resistance, similar to soldering in moderate-temperature cases [3, 20, 21]. However, this method proves troublesome for joining materials with different coefficients of thermal expansion (CTEs), resulting in an interface likely to fail from high thermomechanical shear stress [22, 23]. In addition, many practical situations disfavor the mechanical rigidity of a bonded interface. At high temperatures, some metal foils (e.g., Cu, Al) can be somewhat effective TIMs as they become more ductile and conform to surface asperities more easily. Moreover, the elevated temperature can drive complex elemental interdiffusion processes or reactions between the metal foil and the mating surfaces. This diffusion/reaction is often beneficial to heat transport but unfavorable for

mechanical compliance. For applications in which mechanical compliance is important, metal foams are sometimes preferred over metal foils because their porous structure can withstand considerable strain without transferring excessive mechanical stress [24]. However, the porous structure also drastically reduces the TIM's thermal conductivity and true contact surface area [25].

CNT arrays offer the advantages of low compressive stiffness [13], high thermal conductivity [8], and good thermal and chemical stability [26]. With these properties, if protected by inert atmosphere or vacuum, they can be suitable TIMs for high-temperature applications. In fact, vacuum or inert atmosphere is often required by other device components in order to minimize thermally induced oxidation and sublimation [17, 27]. The benefits of CNT TIMs are expected to be especially prominent for the case of thermomechanically mismatched interfaces because CNT arrays are expected to allow both sides of the interface to expand freely due to their low lateral stiffness and friction [12]. However, experimental evidence to support this argument is lacking to date.

In addition to mechanics, heat transfer is also directly affected by high-temperature environments. The thermal conductivity of an individual single-walled CNT has been shown to decrease with temperature over the 50-550 °C range [9], as is typical for solids as a result of increased inelastic phonon scattering. The overall thermal interface resistance is composed of bulk resistance of the TIM itself and the contact resistances between the TIM and two joining surfaces. Therefore, the impact of temperature-dependent thermal conductivity on the overall thermal interface resistance remains unclear and requires experimental characterization. However, partly due to the lack of a proper test system designed for high-temperature measurements, characteristics of CNT array TIMs have not been reported for temperatures above 250 °C [28]. Here, utilizing a newly developed test rig and its companion data evaluation designed for conducting high-temperature experiments, we measure and report the thermal properties of vertically oriented multi-walled CNT arrays as thermal interface materials at temperatures up to 700°C [29]. Both thermomechanically matched and mismatched cases are tested and discussed.

Experimental

Thermal interface resistance (TIR) is the most important metric to characterize heat transfer between two contacting materials. Testing methods for TIR can be generally classified into two categories: steady-state and transient. A thorough review of various methods along with their advantages and limitations is available in refs. [30, 31]. The most commonly used approach is to generate 1-dimensional (1D) heat flow through one or two well-calibrated meter bar(s), with the tested TIM placed in series. The temperature profile along the meter bar(s) is measured by thermocouples, thermistors, or infrared sensors once the system reaches steady state. Heat flux through the meter bar(s) and the tested TIM can be calculated from the temperature gradient along the meter bar(s) and the thermal conductivity of the meter bar material. Temperature drop across the TIM can be estimated by placing temperature sensors near the interface or by extrapolating from known temperature data points. Subsequently, the TIR of the sample can be determined by simply dividing temperature drop at the interface by the heat flux flowing through it. The principle of this method is well described in ASTM-5470 and other works based on this standard [32].

However, when applied to high-temperature measurements, the foregoing method based on 1D heat conduction faces several challenges. First, the assumption that heat flux is uniform throughout the whole thermal path (i.e., meter bar(s) and the TIM) is not generally valid. Convective and radiative heat losses become significant at elevated temperatures, causing the conductive heat flux to decrease gradually from the hot end to the cold end. Second, the thermal conductivity of the meter bar material should not be considered constant when large temperature differences exist. For example, the thermal conductivity of copper changes more than 12% from room temperature to 700°C [33]. This temperature dependence complicates the heat flux calculation. As described in more detail in Ref. [29], in order to make the 1D bar steady-state method compatible with high temperatures, a redesigned test rig and data evaluation process are required. By conducting the experiment in vacuum, heat loss by convection is eliminated, and the meter bar surface and the TIM sample are protected from oxidation. By fitting the measured temperature profile to the solution of a heat transfer ordinary differential equation (ODE), the effects of heat radiation and temperature dependence of meter bar thermal conductivity can be

accommodated. All the results presented below are obtained from this high-temperature 1D bar test rig.

The test configuration for the two samples studied here are shown in Fig. 1(a) and 1(b), respectively. A vacuum cartridge heater (HeatWave Labs) is located at the top of the test column and used to provide heat input. A bottom chiller with circulating cold water serves as the heat sink. For the thermomechanically matched case, because of size limitations of the CVD chamber, CNT arrays cannot be synthesized directly on the end surface of a Cu bar and therefore were grown on a separate Cu substrate instead. The thermal resistance of one CNT array interface between the Cu substrate and top Cu bar was measured. Measurement of temperature drop across the interface was enabled by an additional thermocouple inserted into the Cu substrate. For the thermomechanically mismatched case, due to the difficulty of drilling a hole in brittle alumina to anchor a thermocouple, CNT arrays were synthesized on both sides of the alumina substrate to create a symmetric interface. The TIR of one CNT array interface is extracted by measuring the total TIR (Cu to Cu), subtracting the bulk resistance of alumina [34] and then dividing the resulting quantity by two. All measurements were performed at a pressure of 0.12 MPa. Notably, the end surfaces of Cu bars are kept fairly rough, with height variation as much as several microns in the 1cm^2 area, in order to replicate a practical situation. Optical profilometry results of the Cu bar surface can be found in Ref. [29].

Fig. 1. Thermal interface resistance test configuration for the thermomechanically matched (a) and mismatched (b) interfaces bridged by vertically oriented CNT arrays. The use of eGRAF in (a), a

commercially available graphite foil, is merely for the sake of preventing diffusion bonding between Cu substrate and lower Cu bar.

For the thermomechanically matched interface, a CNT array was synthesized on one side of an oxygen-free high thermal conductivity (OFHC) Cu substrate (10mm×10mm×2mm, polished with 1500 grit sanding sheet) as already mentioned. First, a five-layer catalyst (10nm Ti, 100nm Ni, 30nm Ti, 10nm Al, 5nm Fe, from bottom to top) was deposited via thermal evaporation. This catalyst was selected to follow previous successful recipes [35]. Next, the Cu substrate was transferred into a MPCVD chamber for CNT growth. At 800°C stage temperature, 10 torr chamber pressure, 50 sccm H₂ and 10 sccm CH₄, and 300W plasma power, the CNT array was grown for 10 minutes. For the thermomechanically mismatched interface, CNT arrays were synthesized on both sides of an alumina substrate (MTI Corp., 10mm×10mm×0.5mm, both sides polished by the vendor). Tri-layer catalyst (30nm Ti, 10nm Al, 5nm Fe) was deposited on both sides of the substrate. CNT growth occurred under the same condition as described above except the substrate was raised by ceramic spacers (0.5 mm thick) to allow for CNT growth on both top and bottom of the substrate.

Results and discussion

Scanning electron microscope (SEM) images of CNT arrays synthesized on Cu and alumina substrates are shown in Fig. 2 (a) and 2 (b), respectively. In both cases, CNTs appear to be vertically oriented. On the Cu substrate, the average array height is approximately 25 μm. On the alumina substrate, CNTs are considerably longer with a height in the 55-75 μm range. This height difference could be attributed to different Ostwald ripening and substrate diffusion rates on the two types of substrates [36]. The CNT array on the top side of the alumina substrate, which faces the plasma during growth, is slightly longer than that on the bottom side, likely because of higher local concentration of carbon species during growth.

Fig. 2. (a) SEM image of CNT array synthesized on a Cu substrate; (b) SEM image of CNT arrays synthesized on both sides of an alumina substrate

The total thermal interface resistance of the Cu-Cu interface bridged by a CNT array as a function of temperature is shown in Fig. 3. The tested interface was thermally cycled from room temperature to a maximum of 700°C and back. At 100°C intervals, the system was allowed to reach steady state, with the temperature profile recorded. Reaching steady state typically required approximately 1 hour. This fully cyclical process was repeated two additional times to verify the repeatability of the observed trend and cyclic stability of the TIM.

Fig. 3. Thermal interface resistance of a one-sided CNT array between two Cu surfaces under thermal cycling.

Total thermal interface resistance generally decreases as temperature increases. In the first cycle, TIR decreases from 126 mm²K/W at 100 °C to 66 mm²K/W at 700°C – a 48% reduction. The trend is generally consistent despite large uncertainty at lower temperatures. An anomalous result was observed in the first heating cycle at 400°C and 500°C. The reason for this anomaly is unclear, as it did not occur in repeated tests on other samples. However, a possible cause is local plastic deformation of the Cu surfaces that may change with temperature due to Cu softening and small relative movements (from local temperature differences). Once this conforming process has completed, the following cycles do not induce further deformation, and the temperature curves become more repeatable. Except for the cases of 400°C and 500°C, TIRs measured during the first cooling stage are lower than those during the first heating stage at each temperature, while the trend with temperature is preserved. Subsequent cycles closely follow the trend and magnitudes of the first cooling stage without significant hysteresis, the absence of which suggests good cyclic stability of the CNT array as a thermal interface material.

As discussed above, the total thermal interface resistance is composed of two parts: bulk thermal resistance and contact resistances at the two ends. Bulk resistance is determined by the CNT array's effective thermal conductivity, which depends principally on volume fraction and array height. The thermal conductivity of a single-walled carbon nanotube is known to decrease with temperature above 75°C [9], and similar behavior has been reported for individual multi-walled carbon nanotubes [10]. We note that the CNTs tested here were grown by MPCVD, which yields higher defect density than CNTs tested in Refs. [9, 10]. The phonon mean free path due to defects should not depend on temperature; therefore the change in thermal conductivity of the present CNTs at high temperature should be lower than that of the CNTs tested in ref. [9], but while still exhibiting a decreasing trend with increasing temperature. Therefore, the bulk thermal resistance of the array would increase with temperature. The effect of temperature on contact resistance was studied by Wang et al. [37] using a molecular dynamics simulation to show that the contact resistance between an individual SWCNT and a Cu surface decreased by approximately one-third from 27°C to 477°C. Notably, Wang et al. [38] measured the thermal contact resistance between CNT arrays and a top diamond-like coating using a 3 ω method in the 7°C -107°C range and also observed a negative temperature-dependence.

Hence, two competing mechanisms that affect the total thermal interface resistance have opposing influences on temperature dependence. Based on the experimental results presented here, the effect on contact resistance is stronger under these conditions. Many studies have attempted to separate and quantify the contributions to total thermal interface resistance between bulk and contact [39-42] using various transient thermal measurements based on the principle that these two resistances yield different transient responses, although the issue remains unresolved [8]. Temperature-dependent measurements can provide an alternative approach to study the relative magnitude of these two resistances, as they have opposing temperature dependencies. The temperature sensitivities of contact resistance and bulk resistance can be estimated from Ref. [9, 37] to be approximately 900 ppm/K and 3500 ppm/K, respectively, in the temperature range 300K-750K. With a lower temperature sensitivity, the decrease of contact resistance still prevails, indicating that the contact resistance is a larger component of the total interface resistance for the tested CNT sample.

The interface between a metal and nonmetal is becoming an increasingly important consideration in a variety of applications, such as thermoelectric devices [17, 19] and high-temperature fuel cells [43]. Direct bonding is often difficult due to highly mismatched thermal expansion coefficients. Even if a joint is successfully fabricated, it is often vulnerable to failure under thermal cycling and shock [23]. Using a mechanically compliant thermal interface material provides an alternative solution when thermal transport is critical and the joint does not bear a large load. An example is the hot-side interface between a dielectric layer and heat exchanger in a high-temperature thermoelectric generator [17, 19].

Alumina is a commonly used dielectric material with low cost and reasonably high thermal conductivity. Its thermal expansion coefficient is reported to be $5.4 \times 10^{-6} \text{ K}^{-1}$ at room temperature [44], much lower than that of Cu ($16.54 \times 10^{-6} \text{ K}^{-1}$) [45]. We use alumina in the present experiments to form a thermomechanically mismatched interface with Cu and to examine the performance of a CNT array in such an interface.

Fig. 4. Thermal interface resistance of a CNT array between alumina and Cu under cyclic conditions.

The resistance shown here is obtained by subtracting the alumina bulk resistance and then dividing by 2.

In Fig. 4, a decreasing trend of TIR with increasing temperature is again apparent. In the first heating cycle, the TIR of one CNT array thermal interface decreases from 127 mm²K/W at 100°C to 93 mm²K/W at 700°C. At all temperatures, the TIR is higher than for the case of the thermomechanically matched interface; this result is expected because of the shorter arrays and better CTE-matching. During the first cooling as well as subsequent cycles, the trend of TIR as a function of temperature closely follows the first heating cycle without significant hysteresis. This observed cyclic repeatability is particularly important considering the drastically different thermal expansion coefficients of the two mating materials. From room temperature to 700°C, the relative displacement of the two substrates can be as high as 40 μm at the sample edges (estimated from their respective thermal expansion coefficients and the sample size). Other TIMs have been reported to undergo thermal cycling degradation related to thermomechanical stress under much milder conditions [46].

Notably, the CNT array is several times taller in this case compared to in the thermomechanically matched interface (55-75 μm vs. 25 μm); however the TIR is only 42%

higher (based on data at 700°C, where uncertainty is the lowest). Considering that the quality and density of CNT arrays (approximately 3% volume fraction), and therefore their thermal conductivity, are similar in both cases as indicated by SEM images, these thermal measurement results suggest that the bulk resistance of the CNT array is not the dominating contributor to the total TIR. If we assume that the contact resistances at the two ends of the array are unchanged between the two cases, the bulk resistance can be roughly estimated to comprise approximately 20% and 40% of the total TIR at 700°C in the short-CNT and long-CNT cases, respectively. At lower temperatures, these percentages are expected to be even lower because of the differing temperature dependencies of bulk and contact resistances.

Fig. 5. Thermal interface resistance of a bare alumina-Cu interface for one temperature cycle.

As a comparison, the interface between Cu and alumina was also tested without a TIM (hereafter referred to as the bare interface), and the results are shown in Fig. 5. The initial TIR is 807 mm²K/W at 100°C, which is more than six times that observed with a CNT array, and subsequently exhibits a predominantly decreasing trend to arrive at 567 mm²K/W at 700°C. The interface is likely to undergo a plastic deformation and/or diffusion bonding at high temperatures,

as the TIR slowly decreases with time. In addition, this decreasing trend of TIR with respect to time is faster at higher temperatures. In this experiment, the tested interface was allowed to sit for 1 hour before data acquisition at each temperature. During the cooling cycle, substantial hysteresis is clearly apparent, supporting the argument that a permanent process (plastic deformation and/or diffusion bonding) has occurred. After the test, the two Cu bars were indeed mechanically attached to the alumina substrate. However, they were still easily separable by the force of a hand, indicating that the bond was not a sound joint, as also suggested by the still high TIR. Systematic studies of these types of diffusion bonding processes can be found in ref. [23].

Fig. 6. (a) Post-mortem SEM image of CNT arrays in the tested Cu-Cu interface; (b) Magnified image of (a); (c) Post-mortem SEM image of CNT arrays in the tested Cu-alumina interface; (d) Post-mortem SEM image of CNT arrays in the tested Cu-alumina interface. Red marks indicate buckling deformation from compressive load. Black marks show the result of lateral stress.

After the thermal cycling tests, morphologies of CNT arrays in both cases were examined under SEM, and related images are shown in Fig. 6. In both cases, the CNT arrays were compressed to shorter thicknesses. In addition, a pressure of 0.12 MPa appears to have caused the arrays to buckle. This observation agrees with previous experimental and numerical studies [14, 47, 48]. Moreover, the free ends of the CNT arrays have formed a dense top mat structure. This

formation indicates that the top of the arrays undergoes more severe deformation than the rest of the arrays, and this result is not surprising considering the lower nanotube density at the top caused by CNT height variation. This top mat conformed to the opposing Cu surface asperities as apparent from the embossed linear striations in Fig. 6(a) that originated from the machining marks on the Cu surface.

CNT arrays in the two cases differ, however, in terms of lateral thermomechanical deformation. For the matched interface, little lateral relative motion occurs between two Cu surfaces during thermal cycling, and consequently the deformation of the CNT arrays appears to be only compressive, without any lateral deformation observed. In the case of CNTs between thermomechanically mismatched surfaces, a more complex mechanical deformation has occurred. We hypothesize that a two-step mechanism results in the final morphologies as shown in Fig. 6(c) and (d). Immediately after the two substrates are forced in contact, CNT arrays buckle under a compressive load (resulting in deformation marked by red lines) and form a top mat that adheres to the opposing Cu surface. Under thermal cycling, the Cu surface shifts back and forth relative to the alumina substrate, which in turn creates a cyclic shear stress in the CNT arrays. This stress induces a secondary lateral deformation of the buckled nanotubes resulting in the final morphology. In Fig. 6(c), the back-and-forth shear movement is signified by the curvature of the arrays marked by the black line. In Fig. 6(d), a staircase-like structure has formed as a result of combined buckling and lateral stretching. CNT arrays in this case did not deform back and forth as in Fig. 6(c), likely because sliding occurred between top of the CNT array and the opposing Cu surface at certain points of the thermal cycle.

Conclusions

In conclusion, we have synthesized vertically oriented CNT arrays as a thermal interface material and for the first time studied their thermal interface properties at temperatures up to 700°C. In a vacuum environment, CNT arrays are stable at the tested temperatures. Furthermore, we have observed that the total thermal interface resistance of CNT arrays decreases with increasing temperature for both thermomechanically matched and thermomechanically mismatched interfaces. This negative temperature dependence is believed to be the result of

reduced contact resistance between CNT arrays and the opposing surfaces. In addition, CNT arrays appear to be robust thermal conductors even when the two mating surfaces undergo significant relative movement. In both cases tested in the present study (Cu-Cu and alumina-Cu), the trend of TIR as a function of temperature is repeatable after three thermal cycles. Post-mortem analysis shows that CNT arrays have buckled but still conform closely to features on opposing surfaces and accommodate thermomechanical mismatch of the two mating surfaces through shear deformation. With these results, we anticipate that vertically oriented CNT arrays will succeed in many thermally and mechanically harsh applications.

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