Vertically Aligned Carbon Nanotubes for Thermal Interface Materials: Quality Control, Alignment Improvement and Laser Flash Measurement

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Abstract

Thermal interface materials based on vertically aligned carbon nanotubes were measured systematically by a laser flash technique. An important modification has been made to the sample structure for the laser flash measurement. Influences of carbon nanotube quality, tip entanglement, alignment and packing density on the overall thermal resistance were discussed.

Introduction

One promising application of CNTs in microelectronic packaging is to use vertically aligned carbon nanotubes (VACNTs) as thermal interface materials (TIMs) to enhance heat dissipation. [1-8] Fabrications and characterizations of VACNT TIMs have been a recent research focus. Hu *et al.* used a 3ω method to test the thermal contact resistance between a 13-μm thick VACNT array and the surface of a free mating substrate. The results showed that the contact resistances were 17 and 15 mm^2 K W^{-1}, respectively, under the pressures of 0.040 and 0.100 MPa. [9] Wang *et al.* used a noncontact technique (photothermal) to measure the thermal conductivity of MWNT arrays but revealed only ~ 27 W/m-K for MWNTs. [10] Ngo *et al.* used electrodeposited copper as a gap filler to enhance the stability and thermal transport of carbon nanofibers. [11] They reported the interfacial thermal resistance of 25 mm^2K/-W under a pressure of 0.414 MPa with a one-dimensional reference bar method. Using a similar characterization method, Xu *et al*. reported a minimum thermal interface resistance of 19.8 mm^2K/W for an VACNT array on a silicon substrate. [1] By using phase change material with VACNTs, they produced a minimum resistance of 5.2 mm^2K/W. Xu *et al*. used a photothermal metrology to evaluate the thermal conductivity of aligned CNT arrays grown on silicon substrates by PECVD. [12] The effective thermal resistance was 12~16 mm^2K/W, which is comparable to the resistance of commercially available thermal grease. Tong *et al*. used a phase sensitive transient thermo-reflectance technique to measure the thermal resistance of the two interfaces on each side of a vertically aligned CNT array as well as the VACNT itself. [2] They concluded that the interface between the free-end CNT tips and the opposing substrate in contact dominated the interfacial resistance. Cola *et al*. fabricated an interface material comprised of a metal foil with CNTs synthesized on both sides of the foil. This fabrication lowered the interfacial resistance to less than 10 mm^2K/W. [13] Furthermore, they grew VACNTs on Si and copper substrates and fabricated them to make a two-sided VACNT TIM layer. By this assembly, they reported a minimum resistance of 4 mm^2K/W. Overally, at least two issues about VACNT TIMs haven't been addressed yet. First, the feasibility of using a laser flash technique to measure the thermal diffusivity of VACNTs is still controversial. Second, convincing experimental results on the influences of CNT alignment, quality (structural defects), tip entanglement (directly related to interfacial thermal resistance) and packing density on the overall thermal resistance of VACNT TIMs are lacking. In this paper, we demonstrated that laser flash could be used to measure VACNT TIMs with acceptable accuracy and sensitivity. Various influences on the thermal diffusivity of the VACNT TIMs were discussed.

Experimental

VACNT Synthesis

Growth substrates for VACNT synthesis were highly doped p-type silicon substrates (1×1 cm^2) with 300-nm-thick silicon oxide by thermal oxidation. 15-nm-thick Al_2O_3 support layer was deposited on the substrate surface by atomic layer deposition, using $Al(CH_3)_3$ (trimethyl aluminum, TMA, Sigma-Aldrich) and distilled water alternatively entrained in nitrogen (Airgas) carrier flow. [14] 2.2-nm-thick Fe catalyst was deposited on the Al_2O_3 support layer by e-beam evaporation at a vacuum of 7.8×10^{-7}-1.1×10^{-6} Torr. Chemical vapor desposition (CVD) synthesis of VACNTs was carried out at 750 ^oC, with the gas flow rate ratio as: $Ar/H_2/C_2H_4$ = 380/150/150 standard cubic centimeter per minute (sccm).[15] A trace amount of hydrogen peroxide was introduced into the chamber for accelerating CNT growth and simultaneously removing surface amorphous carbon. [16, 17] SEM and TEM images of the as-synthesized VACNTs are shown in Figure 1.

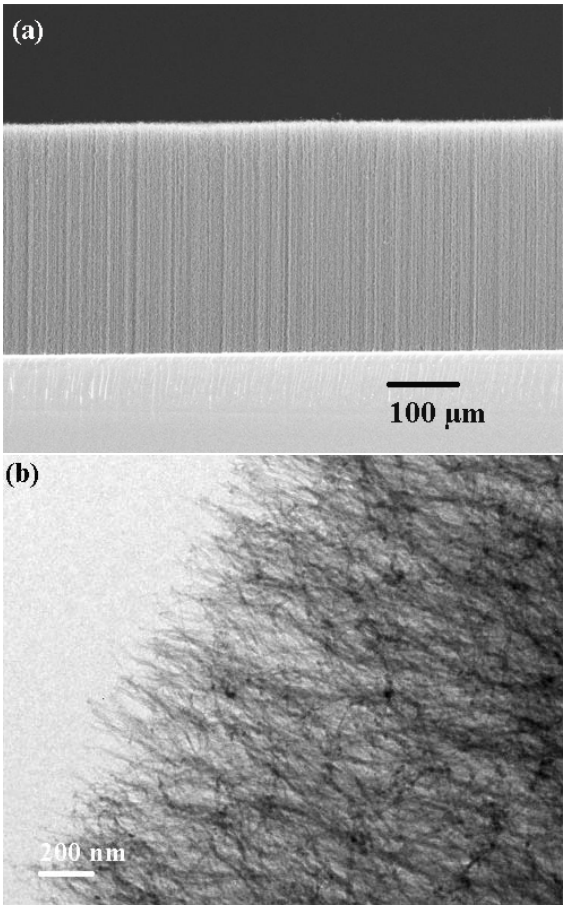
Super-Aligned CNTs

Although the thickness of the VACNTs synthesized by the above-described CVD process is uniform and the alignment is good, the tips of the VACNTs are not well aligned and form entangled network, as shown in Figure 1c. Since the contact between the CNT tips with a mating substrate plays an important role in determining the overall thermal resistance, [6] we synthesized super-aligned VACNTs (s-VACNT) and studied the influence of the VACNT tip entanglement on the TIM resistance. By super-aligned VACNTs, we refer to VACNTs with improved alignment and reduced entanglement at the tips (Figure 1d). Being aware that the entanglement of VACNT tips was attributed to an entanglement-induced

VACNT growth mechansim, [18], we introduced a weak oxidant into the CVD chamber at the growth initiation stage to etch the pre-formed entangled CNT tips. In combination with a sacrificial-layer technique, super-aligned VACNTs were synthesized. [19] In order to further demonstrate the difference in the tip alignment between the s-VACNTs and the common VACNTs, we deposited an Au(300 nm)\Ni(200 nm)\Ti(20 nm) metallization layer on the VACNT tips. As shown in Figure 2, due to the dramatic improvement in tip alignment in the s-VACNTs, the actual thickness of the metallization layer on the s-VACNT surface is much smaller than that on the common VACNT surface though their nominal thicknesses are the same. The difference in the actual thickness of the metallization layer results in completely different wetting behaviors of the CNT surfaces toward water. A thick metallization layer changes the VACNT surface from being superhydrophobic to superhydrophilic due to the dramatically increased surface energy of Au compared to graphitic carbon. In a sharp contrast, the metalized s-VACNTs retain hydrophobic.

VACNTs Densification

VACNTs by conventional thermal CVD techniques show a very low CNT packing density (<9 %). To study the influence of CNT packing density on the overall thermal resistance of VACNT TIMs, we densified the VACNTs 4 times using a mechanical densification process (Figure 3). The as-densified VACNT sample was designated as h-VACNT.



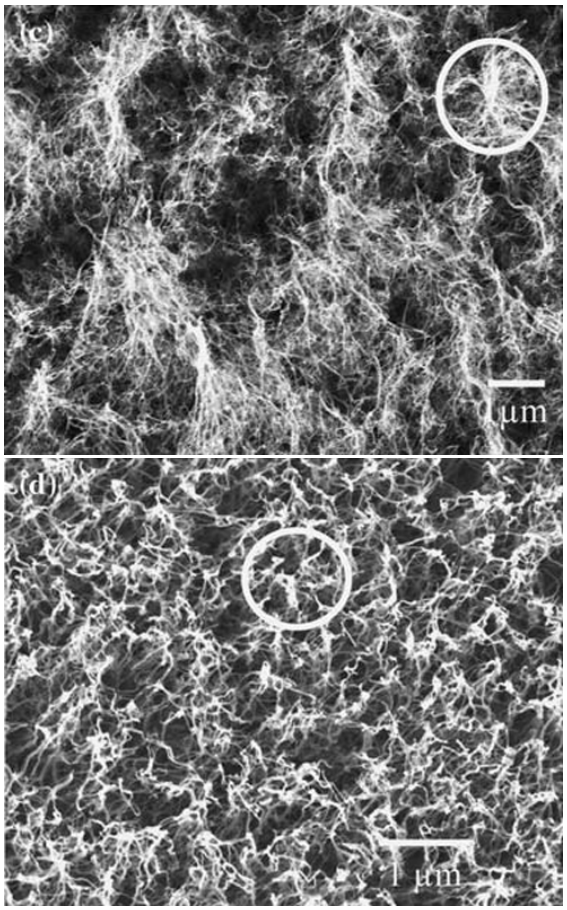


Figure 1. SEM (a, c and d) and TEM (b) images of as-synthesized VACNTs. The circle shows entangled CNTs. (c) Top view of the VACNTs; (d) top view of the s-VACNTs with much better alignment and less entanglement.

Microwave Treatment of VACNTs [20]

Microwave treatment of the synthesized VACNTs was carried out in a variable-frequency microwave (VFM) chamber (MicroCure2100, Lambda Technologies). The microwave system could be programmed to operate at different power levels and duration. Inside the microwave chamber was a self-setup argon-filled glass chamber, in which the VACNT samples were placed. Upon microwave radiation, intensive light emitting, fast heating and outgassing were observed from the VACNT samples. VFM techniques have the advantage of being capable of overcoming the non-uniformities in temperature and arcing associated with traditional microwave processing. In our study, 500 W microwave output was able to heat the VACNT samples above 400 ^{o}C within a few seconds. It has been found that such highly microwave-responsive CNTs could be fast-heated to "super" high temperatures (*e.g.* ~ 3000 K). [21] However, monitoring the actual temperature of the CNTs in the VFM chamber during microwave radiation is extremely challenging since infrared emissivity of CNTs especially at high temperatures is unknown.

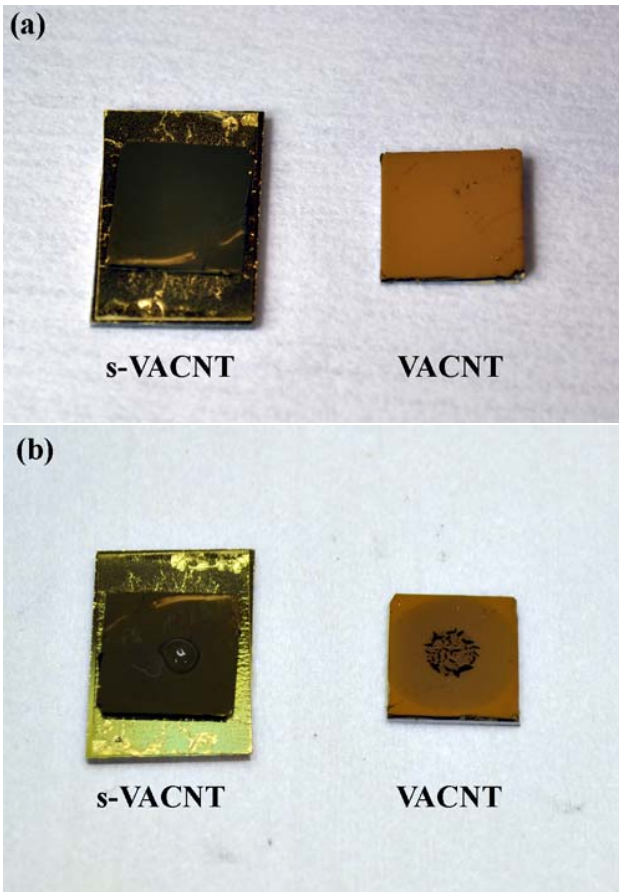


Figure 2. Photographs of the metalized s-VACNT and common VACNT surfaces (a), and their wetting behavior toward water.

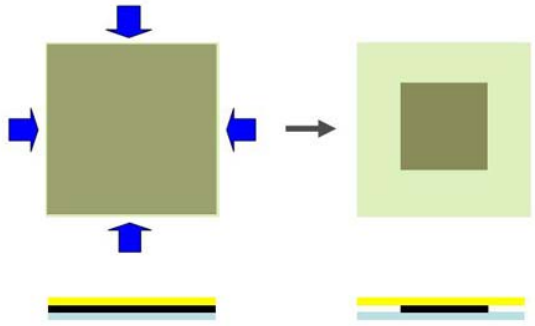


Figure 3. Illustration of the mechanical densification process.

Laser Flash Measurement

Laser flash measurements of VACNT TIMs were carried out in a Netzsch laser flash apparatus (LFA447), with no pressure imposed during measurements. Since a VACNT carpet itself is porous and of very low packing density, the incident laser beam will easily shine into the CNTs and the temperature sensed by the IR sensor convolutes the emission from the sub-top layer. As such, the as-measured diffusivity, as Hata *et al*. pointed out, is an overestimation. [22] To address this issue, a bottom layer of highly thermal conductive material is needed to block, absorb and dissipate the energy of the incident laser beam. However, in a conventional trilayered structure for laser flash measurement, the top and bottom substrates are too thick and sabotage the accuracy of the measurement. [23] Actually, laser flash measurement is based on approximations which were thought to be quite restrictive. In the present study, we modified the sample structure, as shown in Figure 4. [19] This structure has taken into account the following three important issues. [24] First, the small thickness and the high thermal conductivity of the copper foil ensure an extremely short heat transport duration (t_c=0.7L^2/α < 2 μs) through the foil, which, in comparison with the pulse duration (τ=100 μs), is negligible. Second, the lower limit on VACNT thickness is the thickness that ensures the characteristic time (t_c=0.7L^2/α) of heat transport through the VACNTs is larger than the pulse duration (τ=100 μs). Third, the upper limit on VACNT thickness should meet the approximation on radiation loss ($\kappa/\varepsilon L$). A typical raw data curve obtained of a Cu-VACNT-Cu sample by laser flash measurement is shown in Figure 5. It is noted that the as-measured thermal diffusivity is a convolution of the intrinsic thermal property of the VACNT TIM and the two contact interfaces.

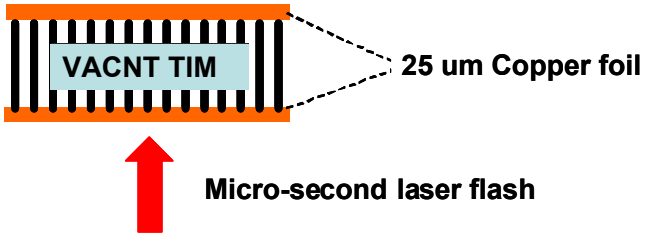


Figure 4. Illustration of the modified structure of a VACNT TIM sample for laser flash measurement.

Other Characterizations

Raman spectra were collected on a LabRAM ARAMIS, (Horiba Jobin Yvon) with a 532-nm-wavelength laser. TGA measurements were carried out in air, using a heating rate of 10 ^{o}C min^{-1}, up to 900 ^{o}C.

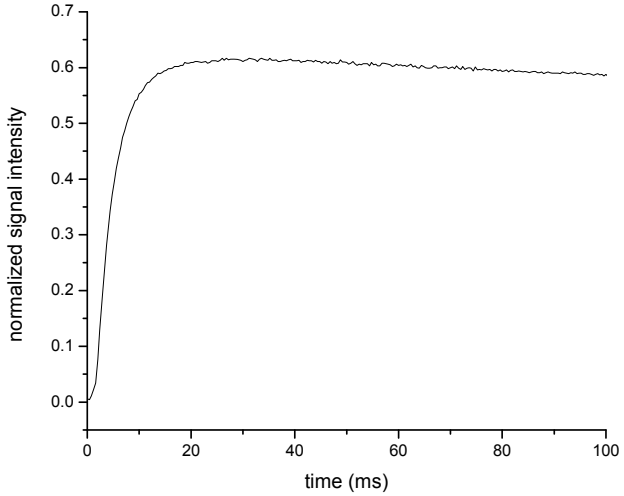
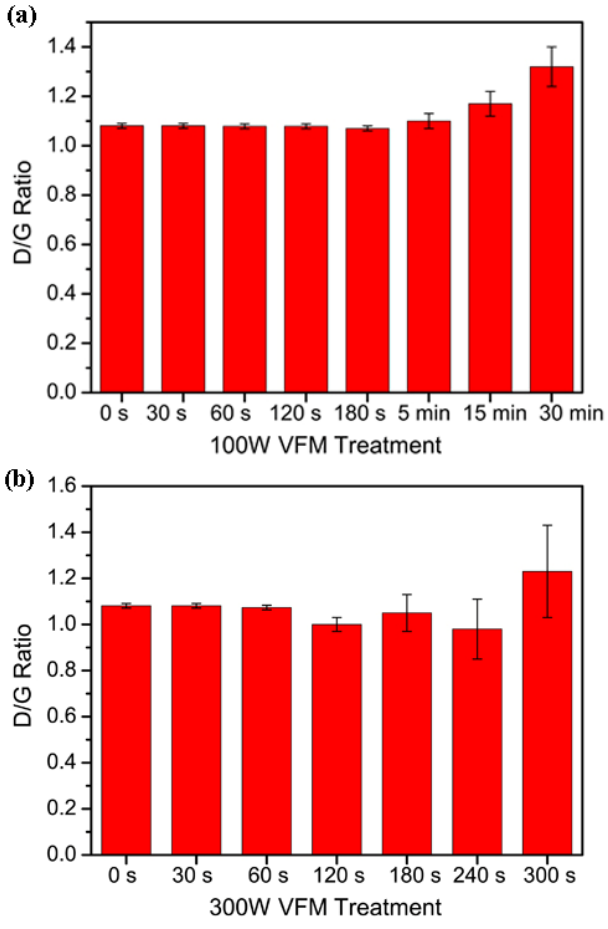


Figure 5. A typical raw data curve obtained of a Cu-VACNT-Cu sample by laser flash measurement.

Results and Discussion

Influence of Microwave Treatment on VACNT Quality (Structural Defects)

Raman scattering is a well-accepted characterization method for evaluating the degree of structural order of MWNTs, by using the ratio of the integrated intensity of D band (I_D) at ~1334 cm^{-1} to that of G band (I_G) at ~1570 cm^{-1}. [25] Also investigated is the ratio of the integrated intensity of D' band ($I_{D'}$, by least-square fitting Lorentzian line shapes to the asymmetric G band in the spectra) at ~1610 cm^{-1} to I_G. [26] Statistical results of I_D/I_G and $I_{D'}/I_G$ for VFM treatments with varied microwave power are shown in Figure 6. It is evident that short duration of VFM treatment with 500 W power is most effective in VACNT annealing. We postulate that what happens during the microwave annealing process is that the defective sites on the synthesized CNTs reconstruct to form graphitic structure, leading to the reduced I_D/I_G and $I_{D'}/I_G$. With extended microwave radiation duration, I_D/I_G and $I_{D'}/I_G$ rise probably due to CNT degradation in microwave or due to CNT oxidation given that a highly effective argon protection is difficult to achieve in the VFM chamber.



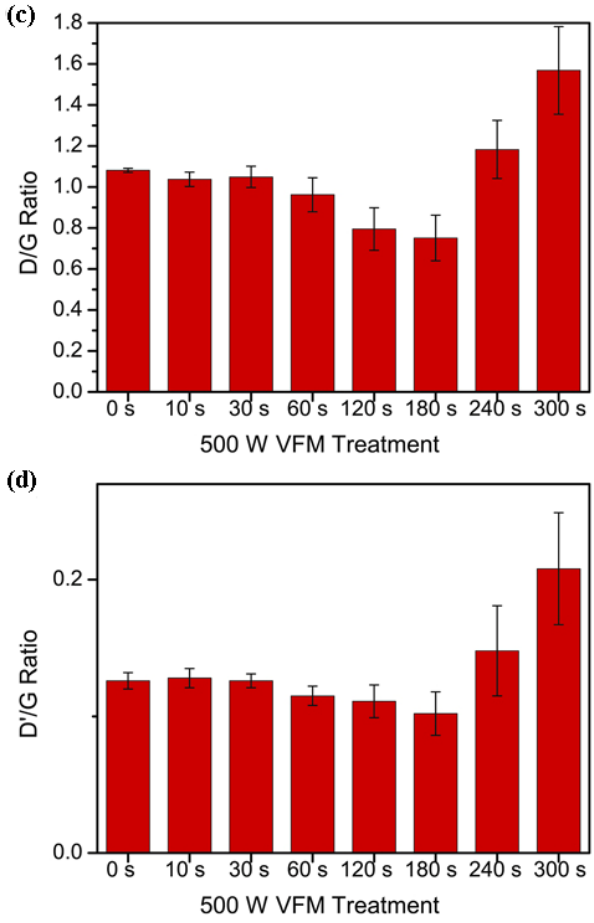


Figure 6. I_D/I_G (a, b and c) and $I_{D'}/I_G$ (d) of the control VACNT sample and the VACNT samples treated by VFM with varied power at varied duration.

Our postulation can be verified by thermogravimetric analysis (TGA) of the VACNTs (Figure 7). TGA has been used widely to study the oxidative stability of CNTs so as to evaluate CNT quality, *i.e.* defect density and purity. In our study, TGA measurements were carried out in air, using a heating rate of 10 ^oC min^{-1}, up to 900 ^oC. For the control VACNTs, the temperature where the derivative weight loss peaks is ~675 ^oC, consistent with the reported values for defective (raw, un-annealed) CNTs. [27, 28] 1 min and 3 min of VFM (500 W) treatments shift the peak temperature up to ~ 730 ^oC and ~740 ^oC, respectively, indicating an effective improvement in oxidative stability, comparable to high-temperature annealed CNTs. In comparison, a 5-min treatment causes a dramatic structural instability. The TGA results show no detectable amorphous carbon or catalyst residue, indicating high purity of our synthesized VACNTs; therefore, the oxidative stability is a reflection of the crystalline defect density of the CNT structure. Increased defect density leads to increased local reactivity to oxygen and, consequently, a lower oxidative stability. Therefore, relatively short microwave radiation duration is effective in reducing the defect density of the VACNTs, while extended duration degrades the VACNTs by introducing more defects.

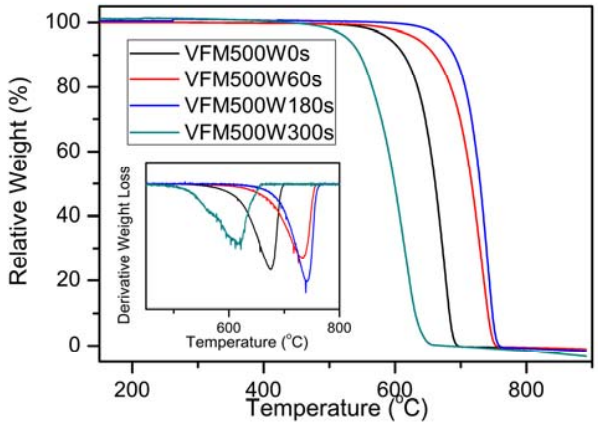


Figure 7. TGA results of the control VACNTs and VFM treated VACNTs; inset is the derivative weight loss plot against temperature.

Table 1. Thermal Diffusivity Results by Laser Flash Measurement

TIMs	averaged thermal diffusivity, α (mm^2/s)
VACNT TIM (350 micron)	8.6
a-VACNT TIM (350 micron)	9.3
s-VACNT TIM (350 micron)	11.9
d-VACNT TIM (350 micron)	4.0
c-VACNT TIM (1/2)	0.9
c-VACNT TIM (1/6)	0.05
h-VACNT TIM (480 micron)	11.1

a-VACNT TIM refers to the VACNT TIM that is made of the microwave-annealed VACNTs (VFM, 500 W, 3 min). d-VACNT TIM refers to the VACNT TIM that is made of the microwave-degraded VACNTs (VFM, 500 W, 5 min). c-VACNT TIM (1/2) and c-VACNT TIM (1/6) represent the VACMT TIMs that are anchored between copper foils and then compressed to 1/2 and 1/6, respectively, of their original thickness.

Influences of VACNT Alignment, Tip Entanglement, Structural Defects and Packing Density on the Measured Thermal Diffusivity

Three factors deal with the intrinsic thermal transport of VACNTs: quality, alignment and packing density. Yi *et al*. measured the thermal conductivity of millimeter-long defective VACNTs. [29] At room temperature, the thermal conductivity of these samples was only ~ 25 W/m-K. However, thermal conductivity recovered to a high value after a high temperature annealing at 3,000 °C. In this study, the influence of CNT quality on the thermal diffusivity of VACNT TIMs is simply evident from the fact that the thermal diffusivity of the VACNT TIM made of the structurally annealed VACNTs is more than twice of that of the structurally degraded VACNT TIM (over-treated by microwave). Compression of VACNTs is detrimental to thermal transport of VACNT TIMs. For example, the c-VACNT TIM (1/6) sample shows two orders of magnitude of decrease in thermal diffusivity. In terms of interfacial thermal transport, CNT tip entanglement plays an important role. The reduced tip entanglement in the s-VACNTs improves the thermal transport effectively. Therefore, it is natural to propose that short but super-aligned VACNTs with high quality and packing density should be desired for TIM applications. To the authors' best knowledge, this is the first time that such a study has been reported. More systematic studies are undergoing.

Acknowledgments

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