Fast and highly anisotropic thermal transport through vertically aligned carbon nanotube arrays

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This letter reports on fast and highly anisotropic thermal transport through millimeter-tall, vertically aligned carbon nanotube arrays (VANTAs) synthesized by chemical vapor deposition on Si substrates. Thermal diffusivity measurements were performed for both longitudinal and transverse to the nanotube alignment direction, with longitudinal values as large as 2.1±0.2 cm²/s and anisotropy ratios as large as 72. Longitudinal thermal conductivities of 15.3±1.8 W/(m K) for porous 8±1 vol % VANTAs in air and 5.5±0.7 W/(m K) for epoxy-infiltrated VANTAs already exceed those of phase-changing thermal interface materials used in microelectronics. Data suggest that further improvements are possible through optimization of density and defects in the arrays.


Individual carbon nanotubes are predicted to have longitudinal thermal conductivities approaching 6000 W/(m K), and measured values of 3000 W/(m K) have been experimentally verified.1,2 Such exceptionally high thermal conductivities originate from the large mean free path for phonons within the atomically perfect carbon networks of idealized nanotubes.3

The ultimate realistic three-dimensional assembly of carbon nanotubes resulting in high thermal conductivity and anisotropy consists of (1) long, continuous nanotubes [Fig. 1(a)] to minimize the thermal resistance at nanotube junctions [Fig. 1(b)], (2) high packing density with minimized bundling, and (3) with few defects and high graphic order for long-range phonon transport. However, attempts to date to assemble short nanotubes into macroscopic fibers,4 papers,5,6 or nanotube composites7–9 have proved inadequate to address these requirements, resulting in thermal properties much lower than that of individual carbon nanotubes. The poor performance of macroscopic nanotube assemblies has been explained in terms of increased phonon scattering at nanotube junctions, inside the bundles, and at the nanotube sidewall defects.

Aligned forests of single-walled carbon nanotubes (SWNTs) have recently emerged as attractive candidates for thermal management, where the problem of phonon scattering at nanotube junctions might be solved.10,11 While reproducible methods to grow long, pure SWNT arrays are still under development, the fabrication of millimeter-long vertically aligned carbon nanotube arrays (VANTAs) containing mixtures of SWNTs and few-walled multiwalled carbon nanotubes (MWNTs) has been achieved through the optimization of chemical vapor deposition (CVD) growth techniques utilizing in situ diagnostics, improved catalysts, and growth modeling.12,13

Here, longitudinal and transverse thermal diffusivities are reported for four samples of millimeter-tall VANTAs illustrated in Figs. 1(c) and 1(d), which were grown by two slightly different CVD techniques.12,13 Details of the experimental setup, catalyst preparation and CVD growth have been described previously.12,13 All VANTAs were grown by acetylene CVD on multilayer metal catalyst films consisting of 10 nm Al, 1 nm Fe, and 0.2 nm Mo deposited by e-beam evaporation on Si wafers at room temperature. However the 6-mm-tall samples VANTA2–VANTA4 were grown with the addition of ferrocene,13 while the 2-mm-tall VANTA1 was grown without ferrocene.12 The flash diffusivity method developed by Parker et al.14 was used to measure the thermal diffusivities of the samples. VANTAs were detached from the silicon wafer with a razor blade and mounted by tapering the sides of the array to the front side of a metal iris diaphragm, which was positioned at 8 mm from the window of a 2×2 mm² liquid nitrogen cooled InSb detector. The VANTA sample was separated from the metal diaphragm by a 2-mm-thick ring of modeling clay (Pasticolor, Ormya). The

![Fig. 1](image-url)
The thermal diffusivities of different VANTA samples were measured at room temperature in air. The thermal diffusivity is calculated from the half rise time of the signal. The anisotropy of thermal diffusivity is defined by the ratio of the longitudinal (0.8±0.2 cm²/s) to transverse (0.011±0.001 cm²/s) diffusivities, and equals 72 for VANTA2. The detector response on the backside of the carbon nanotube arrays oriented longitudinally (h=2.5 mm) and transversely (w=3.4 mm) to the direction of the heat pulse induced. The faster rise time of the detector response for annealed VANTA3, which corresponds to the improved thermal diffusivity of 2.1±0.2 cm²/s compared to that of 0.42±0.06 cm²/s for unannealed carbon nanotubes.

The longitudinal thermal diffusivities of different VANTA samples were measured at room temperature in air varied between 0.42±0.06 and 0.9±0.1 cm²/s. Transverse measurements these dimensions were calculated from the half rise time of the signal. The anisotropy of thermal diffusivity measurements. Thermal diffusivity is defined by the ratio of the longitudinal thermal diffusivity to the transverse thermal diffusivity. The ratio of the Raman tangential G-band intensity to the disorder-induced D band is often used to compare the graphite ordering in carbon materials. The increase in the G to D band ratio has been shown to correlate with higher crystallinity and higher thermal conductivity for carbon fibers. The G/D band intensity ratios were measured at more than ten locations along the length of each cross-sectioned VANTA. For VANTA2–VANTA4 constant G/D ratios of less than 1 were observed and no evidence of the radial breathing modes (RBM) characteristic of SWNTs was found. Sample VANTA1 included some SWNTs as evidenced by the RBM in the Raman spectra, and the G/D ratio increased from 1 to 4 measured from the base toward the top of the array.

The VANTA samples with the lowest thermal diffusivity (VANTA3 and VANTA4) were annealed in argon at 2800 °C for 2 h (Ref. 20) to improve the nanotube crystallinity and gauge the resulting effect on thermal diffusivity. Figure 3(a) shows that after annealing, the Raman G/D band ratios for both samples increased by a factor of 8. The RBM region of the Raman spectrum in the inset of Fig. 3(a) showed no change after annealing, eliminating formation of SWCNT as a possible cause for the observed G/D ratio increase. HRTEM images of nanotubes after annealing in Fig. 3(c) show cleaner sidewalls, fewer sidewall defects and healing of discontinuities at the junctions between nanotube segments with different diameters. We interpret these changes to be responsible for the increase in G/D band ratio. The thermal diffusivity of annealed VANTA3 increased in a range from three to five times. Figure 2(c) shows two detector traces (before and after 2800 °C annealing) for sample VANTA3 mounted with the nanotubes oriented longitudinally. Annealing results in a faster rise time of the signal, indicating improved ther-

[FIG. 2. (a) Schematics showing the orientation of nanotubes in VANTA for anisotropy of thermal diffusivity measurements. Thermal diffusivity is calculated from the half rise time of the signal. The anisotropy of thermal diffusivity is defined by the ratio of the longitudinal (0.8±0.2 cm²/s) to transverse (0.011±0.001 cm²/s) diffusivities, and equals 72 for this sample. (VANTA2). (b) Detector response on the backside of the carbon nanotube arrays oriented longitudinally (h=2.5 mm) and transversely (w=3.4 mm) to the direction of the heat pulse induced. (c) Faster rise time of the detector response for annealed VANTA3, which corresponds to the improved thermal diffusivity of 2.1±0.2 cm²/s compared to that of 0.42±0.06 cm²/s for unannealed carbon nanotubes.

[FIG. 3. (a) Raman spectra of VANTA4 before and after annealing at 2800 °C were measured with the polarization of the 632.8 nm HeNe laser parallel to the orientation of the carbon nanotubes. The ratio of G/D band intensities in the Raman spectrum increases by a factor of 8 as a result of annealing. The inset demonstrates no changes in the RBM region of the Raman spectrum after annealing. (b) HRTEM image of carbon nanotubes in VANTA4 before annealing with sidewall defects. (c) HRTEM image of carbon nanotubes in VANTA4 after annealed showed reduced numbers of sidewall defects.]
diffusivity from 0.42±0.06 to 2.1±0.2 cm²/s for sample VANTA3. The same annealing procedure resulted in a thermal diffusivity increase from 0.42±0.06 to 1.4±0.1 cm²/s for sample VANTA4. These results confirm that the crystallinity of the nanotubes, in addition to their continuity and spacing, is an important factor that affects the thermal properties of the arrays.

The thermal conductivity of VANTA in air $k_{VA}$ was estimated as $k_{VA}=\alpha_{VA}\rho_{VA}c_p$, where $\alpha_{VA}$ is the measured thermal diffusivity, and $\rho_{VA}$ and $c_p$ are the average density and the specific heat capacity of VANTAs and air, respectively. The averaged density and the specific heat capacity were calculated as the sum of the volume ($\delta_{V,\text{VANTA}}$=0.08) and mass ($\delta_{m,\text{VANTA}}$=0.99) fractional densities and the specific heat capacities of these two components, respectively, using $\rho_{\text{VANTA}}=1900±100$ kg/m³, $\rho_{\text{air}}=1.2$ kg/m³, $c_p,\text{VANTA}=470$ J/(kg K), and $c_p,\text{air}=1.0$ kJ/(kg K). The longitudinal thermal conductivities for as synthesized arrays in air were found to be 6.4±0.8, 5.7±0.7, 3.0±0.4, and 3.0±0.4 W/(m K) for VANTA1–VANTA4, respectively. The thermal conductivity increases to 15±2 and 10±1 W/(m K) for longitudinal direction in the annealed VANTA3 and VANTA4, respectively. Despite the high porosity of the arrays, the highest thermal conductivity of VANTAs in air is a factor of 3 higher than that of currently used phase-changing thermal interface materials (PCMs), which consist of a polymer (polyolefins, epoxies, polyesters, and acrylics) mixed with thermally conductive fillers.

Infiltration of VANTAs with epoxy was enabled by the porosity of the arrays. VANTAs were vacuum impregnated with epoxy resin (SpeciFix-40, Struers) and cured for 4 h at 60 °C in a dry box prior to thermal diffusivity measurements. For an epoxy-infiltrated VANTA (8±1 vol %, unannealed, 2-mm-long MWCNT, and Raman G/D band ratio of 3) the same approach was used as described for the VANTA-air composite to estimate [using instead $p_{\text{epoxy}}=1090$ kg/m³ and $c_p,\text{epoxy}=1890$ J/(kg K)] a thermal conductivity of 5.5±0.7 W/(m K). This corresponds to a factor of 20 improvement compared to the thermal conductivity of pure epoxy and a factor of 6.3 improvement compared to previously reported thermal conductivity of VANTA silicon elastomer 706 composite.

In conclusion, we report that VANTAs exhibit higher thermal diffusivity and anisotropy than any other macroscopic nanotube assembly to date. VANTAs are conceptually similar to the idealized structure of material for optimal anisotropic heat transport in Fig. 1(a). Further improvement in the thermal properties of VANTAs is possible through optimization of the growth conditions for arrays which are more crystalline, straight, and dense. The thermal diffusivity of these porous arrays already exceeds that of aluminum and copper, and thermal conductivities reported here for annealed arrays are triple for comparable PCM. Combined with the resilient mechanical performance recently measured for VANTAs, these conformable and springy nanotube assemblies offer unique multifunctional materials for thermal management and sensing applications.
