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Thermal transport barrier in carbon nanotube array nano-thermal interface materials

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A B S T R A C T

Although carbon nanotubes (CNTs) could theoretically achieve thermal conductivity (k_{CNT}) as high as 100 W/m K, the nature of height non-uniformity could induce enormous thermal contact resistance at CNT array-heat sink interface (R_c), obscuring the quality of CNT arrays compared to commercial nano-thermal interface materials (nTIMs). Direct and experimental extraction of the effect of array height uniformity for thermal transport, R_c, provides a foundation for developing an optimum preparation approach of CNT array-based nTIM. However, this remains a big challenge for even the state-of-the-art interface thermophysical measurement techniques. To remedy this situation, we developed a method for achieving experimental distinction between k_{CNT} and R_c. By focusing on growing CNT arrays with height uniformity, instead of the typical method of focusing on increasing the k_{CNT}, we realized the performance boost by eightfold increase in uniformity and elimination of carbonaceous byproducts on the array canopy and dispersed Fe within walls. R_c is successfully cut down by 60% to 1.7×10^{-5} m^2 K/W, while maintaining extremely high k_{CNT} ~170 W/m K is maintained allowing for fast heat transport within CNTs. This study presents novel quantitative evidence that lowering R_c is the most efficient for thermal transport enhancement for CNT array nTIMs.

1. Introduction

Owing to its extraordinary low-magnetic inductance and quantum excitation, carbon nanotubes (CNT) arrays are good candidates for scalable high-performance, high-frequency beyond-silicon electronics circuit worldwide as a potential core technology for achieving 100–200 GHz data processing speed [1–8]. Although CNT arrays outperforms metallic solders in both size shrinkage and better high-frequency electrical signal transmission, low overall thermal conductance prevents its implementation towards interconnector and nano-thermal interface materials (nTIMs) necessities in Very Large Scale Integrations (VLSI). Extremely exciting experimental results of thermal conductivity ~100 W/m K for CNTs have been successively reported [2–5], which thrusts CNT arrays' way into practical cooling application as nTIMs [9–12]. In particular, its newly developed forms, the covalently bonded graphene-CNT (G-CNT) hybrid, multiplies the axial heat transfer capability of individual CNTs, and the extremely enlarged contact area based on graphene, which outperforms the state-of-the-art TIMs by 3 orders of magnitude in heat dissipation [13]. In addition, secondary fillers consisting of metal nanoparticles doped CNTs could provide for efficient phonon transport pathways between main components of TIMs, which renders ultrahigh thermal conductivity (~160 W/m K) and thus contributes to efficient heat dissipation for computer CPU [14].

A series of work done on the systematic synthesis of CNT arrays with remarkable characteristics have been consistently reported, shedding light on the potential for application in efficient thermal management. Pretreatment of catalyst particles prior to CNT

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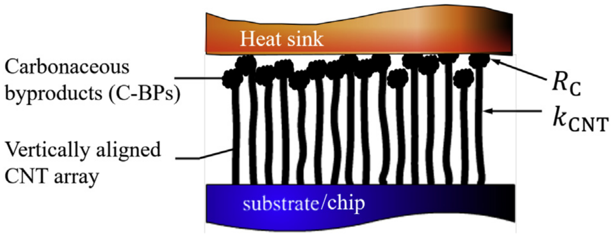

Fig. 1. Two key parameters influencing heat transport for vertically aligned CNT array used as nTIM. (A colour version of this figure can be viewed online.)

growth was first found to be able to optimize the height and alignment of CNT arrays [15]. It was also reported that tuning the growth temperature could bring about variation on the height of CNT arrays, such that higher growth temperature produces large array height [16,17]. Furthermore, Li Q and co-workers found that the height of CNT arrays could also be modulated by controlling the time of continuous feeding the catalyst particles and longer time would results in large array height [18]. In addition, the elimination of undesired byproducts during the growth of CNT arrays, such as aromatic carbon, amorphous carbon, polyhedral carbon and metal particles, is urgent for obtaining better thermal properties of CNT arrays for nTIMs application. A variety of purification methods have been successively proposed to realize the removal of those byproducts [19,20]. Even so, it is commonly reported that the overall thermal conductance degraded to 10^5 W/m^2 K retards CNT arrays implementation as nTIMs. The culprit is the nature of CNT array height non-uniformity, sometimes coated with carbonaceous byproducts (C-BPs), usually graphitic carbon layers enwrapping on Fe nanoparticles and entangled CNTs [19–21], generally exacerbating the non-flatness and inducing large thermal contact resistance at CNT-die or heat sink interface. Thus, a focus on improving array height uniformity should be considered, instead of enhancing the thermal conductivity.

Even for the most state-of-the-art interface thermophysical measurement technique such as Time Domain Thermoreflectance method [22,23], which requires a relatively flat surface for reliable measurements, direct and experimental extraction of the thermal contact resistance at this nanoscale interface is extremely challenging. In this study, we developed an interfacial sensor-based 3ω method for achieving experimental distinction between thermal conductivity (k_{CNT}) and thermal contact resistance at CNT-heat sink interface (R_c), aiming to quantitatively define which plays a more important role in the determination of apparent thermal transport performance of CNT array, k_{CNT} or R_c (Fig. 1).

2. Experimental

2.1. Sample preparation

Vertically aligned multi-walled CNT (MWCNT) arrays with tunable R_c were successfully synthesized based on an approach to modulate array height uniformity by subtly altering catalyst ferrocene ($Fe(C_5H_5)_2$) sublimation temperature (T_{sub}) over a range of 130 °C–180 °C under Floating Catalytic Chemical Vapor Deposition (FCCVD) growth mechanism (see Supplementary Information Content 1 for the details of synthesis) [24–27]. Growth temperature of 800 °C in the tube furnace was selected because it has been proved to be optimum regarding faster growth rate for our experimental system. A He flow of 500 standard-state cubic centimeter per minute (sccm) is used to create an inert environment during the growth. An argon/hydrogen blend (0.95/0.05) at 900 sccm is introduced to carry the ferrocene catalyst particles for eventual deposition on a SiO_2 substrate, and as a carbon feedstock. Owing to the epitaxial growth inhibition of SiO_2, disordered Fe atoms more readily agglomerate into nanoparticle (NP) islands as opposed to a uniformly distributed layer [28]. As shown in Fig. 2A, precipitating C atoms compete for the Fe nucleation sites for diffusing to the backside of the sites for CNT formation. T_{sub} plays a key role in driving the flying of catalyst onto the SiO_2 substrate. In our growth system, lower T_{sub} (135 °C - 142 °C) produces less and rigidly scattered Fe nucleation sites for CNT growth, while higher T_{sub} (≥170 °C) brings more Fe nanoparticles which readily agglomerates to form large nucleation sites (Fig. 2B,D). Typically, smaller Fe nanoparticle diameter leads to the growth of smaller nanotubes, which require fewer carbon atoms for the growth of a unit tubular length, and vice versa [29]. Transmission Electron Microscope (TEM) images validates the differentiated MWCNT dimension phenomena (Fig. 2C,E). The CNT samples grown at T_{sub} = 140 °C comprise ~15 graphene layers while those grown at T_{sub} = 170 °C have ~95 graphene layers, resulting in CNTs remarkably inhomogeneous diameters, a restraint for thermal transport.

2.2. Morphological characterization

Scanning Electron Microscope (SEM) imaging confirmed numerous C-BPs clusters covered the CNT tips for $T_{sub} \geq 170$ °C, their amount gradually decreased until $T_{sub} \approx 150$ °C, and disappeared for $T_{sub} \leq 140$ °C (Fig. 3A–F, for details please refer to Supplementary Information Content 2). Higher T_{sub} generated a higher ferrocene flow rate, and the resulted excessive thermal

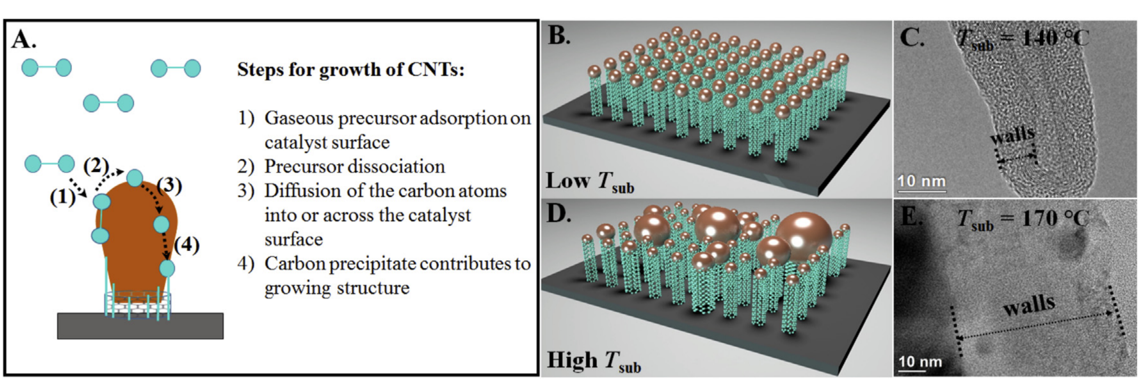

Fig. 2. A. A schematic of growth process of MWCNT via FCCVD method. **B–C.** Illustration for MWCNT array with smaller diameter and more uniform distribution under lower T_{sub}, and the TEM image for the sample grown under T_{sub} = 140 °C validates that case. **D–E.** Illustration for MWCNT array with inhomogeneous diameter distribution under higher T_{sub}, and the TEM image for the sample grown under T_{sub} = 170 °C validates that case. (A colour version of this figure can be viewed online.)