Sensitivity of thermal conductivity of carbon nanotubes to defect concentrations and heat-treatment

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In the present work, we use reverse non-equilibrium molecular dynamics with adaptive intermolecular reactive empirical bond order interatomic potential to investigate sensitivity of thermal conductivity in (6, 6) single-walled carbon nanotubes (SWCNTs) to side-wall defects and high temperature heat-treatment. Effects of two side-wall defect types and their concentrations are evaluated: chemisorbed hydrogen adatoms on the SWCNT side wall and point vacancy defects. The results of the simulations indicate that the degree of hydrogenation and vacancy concentrations have very similar detrimental effects on the thermal conductivity of (6, 6) SWCNTs. Vacancy repair is evident with heat treatment, and heat-treatment temperatures of 3000 °C for up to 22 ns are found to transform point vacancies into various non-hexagonal side-wall defects. The vacancy repair is accompanied by an approximately 10% increase in thermal conductivity. In addition, thermal conductivity measurements in both heat-treated and non-heat treated chemical vapor deposition grown multi-walled carbon nanotubes (MWCNTs) are reviewed. The results of the study suggest that thermal conductivity of carbon nanotubes (CNTs) can be drastically increased if measures are taken to remove common defects from the carbon nanotube side-walls. © 2013 American Institute of Physics.

INTRODUCTION

Significant differences exist in experimental thermal conductivity measurements of MWCNTs. Some of these differences have been attributed to quality of the as-processed CNT specimens, e.g., side-wall defect concentrations due to chemisorbed species and/or vacancy concentrations. The commonly used thermal chemical vapor deposition (CVD) process in the synthesis of CNTs is known to produce a variety of CNT qualities depending on the growth temperature, catalyst, and carbon source gases used.

One of the most promising techniques to identify defect structures in CNTs is use of atomic resolution scanning tunneling microscopy (STM). However, demands of sample preparation and precision required in identifying single defects make such ultra-high resolution techniques unfeasible in characterizing bulk defect densities. As described by Itkis et al., most optical methods utilized in defect characterization in CNTs require a minimum of ~1 pico-gram of sample. However, it has been a challenge to synthesize CNTs with the required degree of homogeneity in these large amounts. Techniques utilizing electrochemical labeling, Raman spectroscopy, and measurement of electrical conductance in identifying a particular form of defect, such as the difference between a single and double vacancy, face similar challenges.

Defects in carbon nanotubes are understood as either the interruption in the $sp^2$ hybridized bonding and/or the presence of physisorbed or chemisorbed species on the surface of the CNTs; defects exist as single to multi-point vacancies, interstitial species, adducts, intercalates between adjacent walls, and amorphous carbon. Carbon interstitials are generally $sp^3$ hybridized carbon atoms bonded between two concentric shells; adducts involve covalently bonded species, such as, oxygen, hydrogen, hydroxyl, and/or phenyl groups, to name a few, and occurs when a single carbon atom rehybridizes to an $sp^3$ conjugation, forming a new bond perpendicular to the $sp^2$ plane; while intercalates are generally adsorbates that exist between two CNT walls. Another common type of CNT defects is non-hexagonal carbon rings that are present within graphene sheets and may contain dangling bonds that are reactive to other functional groups. These non-hexagonal rings are energetically more favorable than point vacancies, and variations, such as pentagon-heptagon (5-7) defects, 5-9 defects, 5-8-5 defects, and paired 5-7 defects (5-7-7-5), which are also referred to as Stone-Wales (SW) defects, constitute the majority of such defects in high quality graphitic materials.

Recently, Chen and McGAUghey used classical molecular dynamics (MD) to estimate formation energy of specific defect types in a 600 nm length (8, 8) SWCNT with 0.1% defect concentration. Their results suggest that adatoms and 5-7-7-5 SW defects require less energy when compared to the formation of single and/or double vacancies. Using non-equilibrium molecular dynamics (NEMD), they showed the predicted thermal conductivities to correlate well with defect formation energies. The study also suggests that lower formation energies are an indicator of a more subtle perturbation of the CNT lattice, and therefore, their presence results in a lower thermal conductivity reduction; 0.1% adatom defects with formation energies of 4.7 eV reduced the thermal conductivity by 25%, whereas single vacancies, with formation energies of 6.9 eV, reduced the thermal conductivity by as much as 40%.
Most CNT synthesis methods utilize transition metals as catalysts, transmission electron microscopy of typical CNT samples has revealed catalyst species to be present at CNT tips, between adjacent walls, and within the hollow center core. Unlike the arc-discharge method, the lower temperatures utilized in typical CVD processes (~600 °C to 900 °C) are unable to vaporize the residual metal catalysts. The residual catalyst materials are found in the form of pure metals, as metal carbides and/or as oxides. Thermogravimetric analysis (TGA) has shown the wt. % of residual non-carbon species to range from 1% to as high as 30%.17,18

The effectiveness and appropriateness of post purification processes used have been discussed in the literature. Gas and liquid phase oxidation combined with filtration to remove smaller carbon species has been found to be less effective when compared to high-temperature vacuum heat-treatment. Carbon samples are found to graphitize during vacuum heating at pressures between 10⁻³ Pa to 10 Pa and temperatures exceeding 2150 °C. MWCNTs, vapor grown carbon fibers, and graphite fibers are all reported to show improved crystallinity (as measured from reduced interlayer spacing) when vacuum annealed to temperatures between 1200–1500 °C. It is understood that a high temperature heat-treatment at temperatures above 1000 °C also has the advantage of removing all oxygen containing functionalities, while non-hexagonal defects and mono-vacancies can become healed at temperatures exceeding 1200 °C.12,16

Bom et al. have suggested that annealing at 2200 °C is likely optimal for removing side-wall defects in MWCNTs, since little improvement is gained in the oxidative stability of samples using higher heat-treatment temperatures. Inductively coupled plasma-optical emission spectroscopy data also suggest that heat-treatment significantly decreases residual Fe catalyst from MWCNTs. Annealing temperatures above the vaporization temperature of Fe, i.e., 1800 °C, are found to remove the majority of Fe content. Huang et al. have compared HCl and HNO₃ acid treatments to high temperature vacuum heat-treatments up to 2150 °C. Using energy dispersive spectroscopy (EDS) and TGA data, they suggested acid treatments with HCl and HNO₃, or combinations of both, reduce residual catalyst content and improve SWCNT purity from 89% to no more than 92%. They also suggested that lower acid soluble oxides, such as Al₂O₃, are more readily removed with lower vacuum pressures of 10⁻³ Pa when compared to 10 Pa. Huang et al. also found by using gas phase oxidation tests, i.e., burn tests in atmosphere, that acid treated specimens had lower combustion temperatures, suggesting a larger abundance of side-wall defects. While acid treatments have been found to remove residual catalysts, Raman spectroscopy data suggest that vacuum heat treatment above 1800 °C is capable of not only removing metal catalyst but also repairing sidewall defects to improve overall graphitization. Moreover, in Huang’s study, TGA analysis determined that the samples tested did not contain detectible amounts of amorphous carbon. For this reason, it was believed that the improved D to G Raman ratio was a result of side-wall defect repairs and not loss of amorphous carbon.

High temperature vacuum (or inert gas) heat-treatment is understood to be an attractive purification method due to its ability to effectively remove residual catalyst material and also heal minor side-wall defects. For this reason, this paper utilizes molecular dynamics simulations to investigate how high temperature (up to 3000 °C) heat treatment affects thermal conductivity of SWCNT. Defect concentrations in SWCNTs are investigated since they are the simplest form of carbon nanotubes. Moreover, affects of varying concentrations of chemisorbed hydrogen on thermal conductivities of SWCNTs are investigated since hydrogen adatoms are the simplest representation of more complex functional groups commonly left behind by gas and liquid phase post-growth oxidation treatments.

METHODS
Reverse non-equilibrium molecular dynamics (RNEMD)

Several classical MD techniques, such as the NEMD, “Müller-Plath” RNEMD, “Green-Kubo” EMD, and homogeneous nonequilibrium molecular dynamics (HNEMD), have been widely used to obtain thermal conductivity of atomic structures. In the present study, thermal conductivity is obtained using the RNEMD method.25 Figure 1 is a schematic showing the principle of the RNEMD technique. The technique involves imposing a heat flux and measuring the resulting temperature gradient. RNEMD algorithm first divides the simulation domain into N bins along the direction in which the thermal conductivity is to be estimated. Atoms do not recognize the existence of the bins and are permitted to pass from one bin to another. The temperature of kth bin, T_k, is measured by averaging the kinetic energy of the n_k atoms in the kth bin over a time t_{avg}

\[ T_k = \frac{1}{t_{avg}} \sum_{t} \left[ \frac{1}{3k_B} \sum_{i=1}^{n_k} m_i v_i^2(t) \right]. \]  

A heat flux is imposed by exchanging the velocity vectors of the “hottest” atom in the lth slab with the “coldest” atom in the N/2 slab. The heat flux has the form

\[ \mathbf{q} = \sum_{transfers} \frac{1}{2} \mathbf{m} \left( v_h^2 - v_c^2 \right) \frac{2tA_c}{2tA_c}, \]

where the subscripts h and c denote the hot and cold atoms, t is the time span over which the transfer of energy occurs (on the order of the MD time step), and A_c is the cross-sectional area. The heat flux in the sample is equal to half of the rate of energy exchange. The applied transfer of energy occurs during time integration with micro-canonical ensemble (NVE), such that the total energy of the system is conserved.

Adaptive intermolecular reactive empirical bond order (AIREBO) potential, which is implemented in LAMMPS simulation code, is used as the interatomic potential. The AIREBO is an extension of the reactive empirical bond order potential (REBO), which is a Tersoff-style potential used to model covalent bonds within hydrocarbon systems. The
AIREBO and REBO potentials are considered to be reactive potentials capable of modeling the formation and breaking of covalent carbon-carbon bonds when two atoms are separated by a cut-off distance of less than 2 Å. The hybridization states of the bonded atoms are modeled by the strength of the potential depending on the local coordination number of each atom. The AIREBO formulation is built off of the REBO formulation by the addition of a pair-wise Leonard Jones component, \( E_{LJ}^{ij} \), and a four atom dihedral torsional component, \( E_{TORSION}^{ijkl} \), such that the potential energy of any particular atom has the form

\[
V = \frac{1}{2} \sum_i \sum_{i'j} \left[ E_{REBO}^{ij} + \sum_{i'jk} E_{TORSION}^{ijkl} + E_{LJ}^{ij} \right],
\]

where the first term, \( E_{REBO}^{ij} \), is the bonded interaction first developed by Brenner in 1990 and later reformulated in 2002, which is also referred to as the "2nd generation REBO potential." The 2nd generation REBO potential contains an improved description of carbon-carbon bond energies, lengths, and force constants and has resulted in improved predictions of the elastic properties of diamond and graphite. The addition of \( E_{TORSION}^{ijkl} \) includes the potential energy due to the stiffness of dihedral bond planes and is understood to better model hydrocarbon chains with improved accuracy. The Lenard-Jones term, \( E_{LJ}^{ij} \), models long range non-bonded interactions, such as those existing between adjacent sheets of graphene or MWCNT layers.

Sample preparation

A custom MATLAB script is used to create the LAMMPS input *.data file by reading the coordinate locations of a pristine SWCNT listed in a *.xyz file. The *.xyz file is built using the theoretical and computational biophysics group’s visual molecular dynamics (VMD) software nanotube builder. To create structures having initial vacancies, atom identification numbers are selected at random and deleted from a compiled list. Once a specified percentage of atoms are deleted, the existing structure is duplicated. One of the duplicated parts is translated along the axial direction of the other, such that the resulting structure is twice the length of the original. Because the RNEMD algorithm creates the hot bath in the center of the final structure, duplication of the structure permits two identical samples to be tested per MD run. In addition, using the *.xyz file formed from VMD, hydrogenated SWCNTs are formed by placing a hydrogen atom at randomly selected carbon atoms. The hydrogen atoms are placed 1 Å away in the radial direction from the randomly selected carbon atoms.

A one femtosecond time step is employed for all simulations. To get well-equilibrated simulation structures with vacancies and added hydrogen atoms, a potential energy minimization routine is performed, followed by 10 ps of time integration with microcanonical ensemble (NVE) and heat-treatment process, where applicable. Each structure is brought to its specified temperature using a minimum of 100 ps of time integration with canonical ensemble (NVT). NVT integration allows for the control of the simulation box temperature by Nose-Hoover style non-Hamiltonian equations of motion. Samples selected for the "3 ns heat-treatment" were subjected to 1 ns of NVT integration to elevate atom temperatures to 1073 K, 1773 K, or 3273 K. Using an NVT ensemble, the temperatures are thermostated to maintain the temperature of interest for an additional 1 ns. A 1 ns NVT integration is subsequently used to cool atom temperatures back to 300 K. Considering heat-up, maintaining, and cooling, the heat treatment procedure totals 3 ns. Following cool-down, the potential energy of the samples is monitored for 10 ps of the NVE integration time to ensure the potential energy of the system remains constant.

During NVT integration, the system pressure can inadvertently increase due to thermal expansion of the SWCNT against the computation domain boundaries. In this regards, 100 ps of isothermal-isobaric time integration (NPT) are performed on all samples to control the temperature while adjusting the size of the computational domain. Once the simulation boundaries are readjusted to reduce pressure on the sample ends, the integration scheme is switched to NVE so that the volume and total energy remain constant during the thermal conductivity measurement algorithm.

Bin sizes (Fig. 1) are selected such that each bin is approximately 3 lattice constants in length along the direction in which the thermal conductivity is computed. Temperature gradient measurements are made by spatially averaging the temperature profile of all atoms in each bin. The resulting temperature is additionally time averaged over 10 ps to act as a noise filter. Unless otherwise noted, temperatures are recorded every 100 ps for 2 ns to ensure that the temperature distribution has reached steady state.
To determine whether additional heat treatment affected thermal conductivity, a select number of 10 nm length samples (20 nm once doubled) were subjected to an additional 22 ns of heat treatment. In place of the 3 ns treatment procedure, the sample temperatures are elevated to 3273 K using 2 ns of NVT integration. Once the average system temperature reaches 3273 K, an additional 18 ns of NVT integration is applied, followed by 2 ns of NVT integration to return the atoms to 300 K. 10 ps of NVE integration is subsequently used to ensure that the potential energy of the structure is minimized.

The creation of random vacancies in a \( sp^2 \) hybridized sheet of carbon atoms has the possibility to create dangling bonds, especially at di- and tri-vacancy sites. Chemically reactive dangling carbon bonds may act as chemisorption sites for non-carbon species. The bonding of non-carbon species to the SWCNT side-wall will later be shown to affect thermal conductivity. As will be shown later, heat-treatment is capable of restructuring the carbon network into alternative structures that may be free of dangling bonds. To the author’s knowledge, to date, the effect of dangling bonds on thermal conductivity has not been quantified. As a first approximation, dangling bonds are not considered in the present thermal conductivity results.

**RESULTS**

In pristine SWCNTs, the only source of phonon scattering is phonon-phonon scattering and possible boundary scattering at the ends of the sample. Consequently, in short and pristine CNTs generally used in MD simulations, the mean free path due to phonon-phonon scattering is greater than the sample length, and thus the effective phonon mean free path is restricted by the sample length. This length dependent thermal conductivity of SWCNTs is a result of ballistic or semi-ballistic phonon transport in the relatively short length CNTs. With increasing sample length, the phonon thermal conductivity continuously increases before converging to its intrinsic value (as governed by the phonon-phonon mean free path), resulting in length independent (diffusive) thermal conductivity.

Figure 2 depicts the temperature profiles of a representative (6, 6) SWCNT as measured using RNEMD. The existence of temperature slips in the pristine sample at the center (location of hot bath) and ends (locations of cold baths) suggests semi-ballistic phonon transport. The temperature profile resulting from ballistic phonon conduction cannot be predicted from the temperatures of the hot and cold baths using \( (T_h - T_c)/L \). For this reason, thermal conductivity is calculated from the temperature gradient of the linear region (shown as solid black lines in Figure 2) and the imposed heat flux occurring from the velocity swapping algorithm (Eq. (2)). For heat transfer to be diffusive, the sample length must be larger than the dominant phonon mean free path.

**Effect of chemisorbed hydrogen**

The thermal conductivity of (6, 6) SWCNT is obtained as a function of chemisorbed hydrogen atoms on the outer-wall surface of the CNTs. Simulations are performed on a 50 nm simulation box length, i.e., 25 nm sample length, for hydrogen adatom concentrations varying from 0% (pristine) to 5%. The state of hybridization of the carbon atoms chemically bonded to the hydrogen atom changes from \( sp^2 \) to \( sp^3 \). This change in hybridization alters the bond angle to be closer to 109.5° (Fig. 3, inset), effectively “lifting” them from the nanotube axis.

Figure 4(b) shows the measured thermal conductivity as a function of concentration of hydrogen/phenyl group in a 25 nm length (6, 6) SWCNT. The hydrogen adatom data are normalized with the thermal conductivity of pristine (6, 6) SWCNT.
with a 25 nm length. These data suggest that thermal conductivity is extremely sensitive to alterations in the carbon network and is reduced by nearly 20% with only 0.2% hydrogen adatoms. A 2% concentration of hydrogen adatoms reduces the thermal conductivity by approximately 60%. Padgett and Brenner\textsuperscript{31} have reported similar sensitivities in the case of the chemical functionalization of SWCNTs using chemisorbed phenyl groups. In their study, RNEMD simulations were performed using a similar 2nd generation REBO potential on a (10,10) SWCNT of 30 nm length. The data presented for the phenyl groups are normalized by the thermal conductivity of pristine (10,10) SWCNT of 30 nm length, taken from Padgett and Brenner.\textsuperscript{31} The data shown in Fig. 4(a) further substantiate the extreme sensitivity of SWCNT thermal conductivity to concentration of adatoms and carbon re-hybridization. It is also important to note that the (10,10) SWCNT has a 1.36 nm diameter, while a (6,6) SWCNT has a 0.81 nm diameter. Comparison of Padgett and Brenner\textsuperscript{31} data on (10,10) SWCNT to the (6,6) SWCNT may suggest that thermal conductivity reduces more rapidly in smaller diameter SWCNT with increasing adatom concentration. However, due to the differences in interatomic potentials used in the two studies, further study is necessary to determine the sensitivity of thermal conductivity to adatom concentration as a function of CNT diameter.

In addition, thermal conductivities of different sample lengths were calculated for pristine SWCNTs and SWCNTs with 0.25%, 1%, and 5% hydrogen adatoms. Plotted in Figure 4(b) as the solid diamonds is the calculated thermal conductivity for a pristine (6,6) SWCNT as a function of nanotube length used in the simulations. The thermal conductivity increases with increasing CNT length up to a length of at least 400 nm, where a thermal conductivity of $250 \pm 20 \text{ W/mK}$ is estimated. This value represents length convergence, and is therefore considered to be the lower limit of thermal conductivity for an isolated (6,6) SWCNT. The result also suggests that the phonon scattering length is longer than about 400 nm. Mingo and Broido\textsuperscript{32} have shown that the second and other higher-order 3-phonon processes are sufficient at scattering the long wavelength phonons to cause convergence of thermal conductivity with increasing sample length. Comparison of the values obtained for the pristine (6,6) SWCNT to NEMD literature indicates that the AIREBO potential predicts thermal conductivities that are up to 30% lower than that of the similar REBO formulism\textsuperscript{33} and up to 65% lower than the Tersoff potential. For example, Chen and McGaughey\textsuperscript{11} determined a length independent thermal conductivity of a pristine (8,8) SWCNT to be 284 W/m-K at 600 nm, which is 28% lower than a previous prediction that utilized the REBO potential for the same structure.\textsuperscript{33} The non-bonded and dihedral interactions that are included in the AIREBO potential possibly increase phonon-phonon interactions that exacerbate Umklapp scattering.

FIG. 4. (a) Thermal conductivity as a function of hydrogen adatom concentration for a 25 nm (6,6) SWCNT. Thermal conductivity is normalized by the value of the pristine (6,6) SWCNT sample of 25 nm length, 124 W/m-K. Also shown is the effect of chemisorbed phenyl groups on a (10,10) SWCNT as measured using RNEMD from Padgett and Brenner.\textsuperscript{31} Thermal conductivities for the case of chemisorbed phenyl are normalized by the value of the pristine sample of (10,10) SWCNT of 30 nm length, 104.7 W/m-K. (b) Thermal conductivity versus nanotube length for various degrees of hydrogenation. Diamonds 0%, open squares 0.25%, solid circles 1%, and solid triangles 5% hydrogenated.

Also plotted in Figure 4(b) is the thermal conductivity estimated for three hydrogen adatom concentrations studied. The hydrogenated CNTs all show significantly smaller thermal conductivities that converge well with respect to nanotube lengths greater than about 200 nm. The faster convergence implies a much shorter scattering length for phonons in the hydrogenated CNTs compared to those in the pristine structure. The simulations predict a decrease in thermal conductivity of at least a factor of 2 with as little as 1.0% of the atoms in the CNT being hydrogenated. Hydrogenation of 5% continues to degrade the thermal conductivity, but to a much lesser degree compared to the drop from a pristine to 1.0% hydrogenation.

**Effect of vacancy defects**

Plotted in Figure 5 is the thermal conductivity of pristine (6,6) SWCNT and (6,6) SWCNT with 1% and 2% vacancy concentrations as a function of increasing sample lengths. These vacancies were created within the SWCNT
crystal structure using the random function generator available in MATLAB. Consequently, the majority of the vacancies generated were mono-vacancies with a few di-vacancies. As discussed in Figure 4(b), the pristine SWCNT specimen shows a slowly converging thermal conductivity, with convergence estimated to occur at ~400 nm. The presence of defects is expected to reduce the length over which thermal conductivity convergence takes place, and samples with 1% and 2% vacancies are found to show convergence at sample lengths near 25 nm. This length convergence is strikingly similar to the length convergence reported by Padgett and Brenner for the chemical absorption of 1% and greater phenyl group concentrations on the exterior of a (10, 10) SWCNT.31

From Fig. 5, the intrinsic thermal conductivity of a pure (6, 6) SWCNT is estimated to be 250 ± 20 W/m-K. The SWCNTs with 1% and 2% vacancy defects has a thermal conductivity of 43 ± 2 W/m-K and 28 ± 1 W/m-K, respectively. These values suggest that 1% vacancy defects will reduce thermal conductivity in small diameter SWCNTs by nearly 83%, whereas 2% vacancy defects are found to reduce thermal conductivity by 88%.

### Effect of heat treatment on thermal conductivity

As suggested by SWCNT phonon dispersion relations, vibrations of approximately 100 THz must be accurately resolved to model atomic motion. This requires the conventional MD time step to be on the order of a single femtosecond. Even with fully parallelizable MD algorithms and supercomputers with banks of multi-core processors, the total times for molecular dynamic simulations are limited to tens of nanoseconds. The MD nanosecond time span contrasts with commonly used annealing heat-treatment procedures by nearly 12 orders of magnitude, which generally involves hours of high temperature heat-treatment.15,18 Time scales on the order of hours are currently unattainable with classical molecular dynamics. However, using classical MD, the current study shows that thermal conductivity improves with only nanoseconds of the heat treatment in SWCNTs with previous vacancies.

Figure 6 depicts the same (6, 6) SWCNT with 3% vacancies in three stages of heat treatment. Figure 6(a) shows the relaxed structure following an algorithm that minimizes the total system potential energy.26 With increasing temperature heat-treatment, a greater majority of the vacancy sites are reformed into non-hexagonal defects. The 3273 K, 22 ns, heat treatment is found to replace all vacancy sites with multiple forms of side-wall defects. The formation of 5-8-5 defects occurs following the 3 ns of MD simulated heat treatment at 1073 K, with a greater majority forming at higher heat-treatment temperatures.

Based on a simple valence argument, di-vacancies have the ability to become restructured into pentagon-octagon-pentagon structures (5-8-5) that are free of dangling bonds, while single vacancies are found to result in pentagon-decagon (5-10) and heptagon-heptagon (7-7) defects. Because Stone Walls (SW), (5-7-7-5) defects do not require stress concentrations. Moreover, comparison of the atomic positions of the heat-treated structures to the original structures indicates that the formation of SW defects is found to occur by bond rotations near vacancy sites to relieve local stress concentrations. Hence, comparison of the atomic positions of the heat-treated structures to the original structures indicates that the formation of SW defects is found to occur in samples containing vacancies that are heat-treated at temperatures exceeding 1773 K. Comparison of the locations of the vacancy sites prior to and following heat treatment suggests that the 22 ns heat treatment either mobilizes or heals single vacancies.

Figure 7 shows the thermal conductivity normalized by that of the pristine SWCNT as a function of original vacancy concentrations. The results suggest that heat treatment at 1773 K for 3 ns increases thermal conductivity by no greater than 5%, while heat treatment at 1073 K for 3 ns has negligible improvements over the specimens with original vacancies. Annealing at higher temperatures may increase thermal conductivity by approximately 10% for all vacancy concentrations. Because higher heat-treatment temperatures are found to replace vacancies with non-hexagonal side-wall defects, the results of this study suggest that non-hexagonal defects are a milder form (require less energy of formation) of point defects since carbon-carbon bonding is restructured rather than terminated. This finding is in agreement with NEMD thermal conductivity measurements of specific forms of non-hexagonal side-wall defects.11

The standard deviations reported in Fig. 7 are determined by the error in the measured linear regression of the temperature distribution. With small defect concentrations, there is greater error in assuming a single linear temperature profile. If the distance between defects is smaller than the phonon-phonon mean free path, phonon transport between defects is ballistic (Fig. 8). In this scenario, the conventional definition of a thermal conductivity that describes the entire sample may not apply, since a single temperature gradient is increasingly difficult to identify. SWCNTs with few numbers of point defects may be better modeled as multiple samples having individual local temperature gradients. Figure 8(a) shows the measured temperature profiles of a (6, 6) SWCNT with 1% vacancies compared to the same SWCNT (Fig. 8(b))...
treated with the 22 ns heat treatment process. The heat fluxes are 280 nW, 326 nW, and 306 nW, for Figs. 8(a)–8(c), respectively. When phonons are scattered from defects, a step in temperature, $\Delta T$, indicates an increase in thermal resistance. Since the heat flux, $q$, is known from Eq. (2), the thermal resistance of a defect can be estimated using

$$R_{th} = \frac{\Delta T}{q}. \quad (4)$$

As shown in Figs. 8(a) and 8(b), temperature steps are clearly identifiable. These temperature steps correspond to thermal resistances of $5.35 \times 10^7$ K/W and $6.78 \times 10^7$ K/W for the non-heat treated SWCNT and $9.82 \times 10^7$ K/W for the heat-treated SWCNT. It is important to note that hydrogen adatoms do not produce the temperature steps due to ballistic phonon transport between absorption sites like those produced due to the presence of vacancies (Figs. 8(a) and 8(b)). Instead, gradually diffusive behavior occurs with increasing adatom concentrations.

The mobility and coalescence of defects is expected to result in an increase in the purity of the SWCNT segments between the unhealed defects. Ballistic transport is expected to be more prevalent within higher purity segments, which results in increased boundary scattering at the existing defect locations. As each defect is expected to contribute to the thermal resistance of the sample, the overall effective thermal resistance of the SWCNT is understood to decrease with heat-treatment. Figures 8(a)–8(c) illustrate that the calculation of an effective thermal conductivity/thermal resistance is unreasonable at low defect concentrations due to the nonlinearity in the overall temperature profiles of the sample. The large uncertainties in reported thermal conductivity values for samples with 0.5% and 1.0% vacancy concentrations reflect the standard error in the linear regression identified as option 1, in Figs. 8(a) and 8(b). Figures 8(a) and 8(b) show the same SWCNT both before and after heat-treatment. The shift in the position of the temperature steps is evidence of vacancy mobility and healing. Higher defect concentrations reduce the inter-defect spacing resulting in more diffusive type thermal transport (Fig. 8(c)) in the SWCNTs.

Classical MD is effective at identifying the existence of ballistic phonon transport. If the thermal conductivity of the structure is determined from the temperature gradients between the defects, i.e., linear regression option 2 in Figs. 8(a) and 8(b), the calculated thermal conductivities exceed the limit of ballistic thermal conductance by nearly 5-fold. The results of this study suggest that as the length of the samples approach the ballistic lengths, thermal conductivity calculations are better left to spectral methods that calculate thermal conductivity directly from phonon dispersion and relaxation times of various phonon modes.

Figure 9(a) shows the transformation of initial vacancy defects in a (6, 6) SWCNT of 10 nm length with 3% initial vacancy concentration after a high temperature heat-treatment at 3000°C for 3 ns, 5 ns, 10 ns, and 22 ns, respectively. The initial vacancy concentration was generated by using a random function algorithm available in MATLAB and comprised of 40 mono-vacancies and 8 di-vacancies. With heat-treatment, these vacancies were transformed into a combination of interstitial, 5-7, 5-7-7, 5-7-7-5, 5-7-7-7, 5-7-8-5, 5-7-8-7, 5-7-9-5, 5-7-9-8, 5-7-9-9, 5-7-9-7-8, 5-7-9-7-9, 5-7-9-7-9-8, and 9 type defects. The evolution of the number of each defect with heat treatment time is shown in Figure 9. It is interesting to note that some of the initial sidewall vacancy defects were converted to out of plane interstitial defects with a dangling bond after 5 ns and 10 ns following the high temperature heat treatment. However, after
22 ns, these interstitial defects were all converted to non-hexagonal side-wall defects. Also, it is interesting to note that with an increase in heat treatment time, the number of defects decreased from initial 48 side-wall vacancy defects to 22 side-wall non-hexagonal defects.

The evolution of overall (effective) thermal conductivity of the (6, 6) SWCNT with heat treatment time is shown in Figure 9(b). The thermal conductivity increases from 15.5 W/m-K to 20.8 W/m-K to 25.6 W/m-K to 27.3 W/m-K after 5 ns, 10 ns, and 22 ns heat treatment time at 3273 K.

Alteration in phonon dispersion with side-wall defects

The three important mechanisms that are understood to influence thermal transport in the SWCNTs under consideration include (1) magnitude of phonon frequencies; (2) phonon group velocities; and (3) phonon relaxation times. Defects reduce thermal conductivity by limiting phonon mean free path, thus reducing phonon relaxation times. However, the question remains whether defects alter phonon dispersion in SWCNTs? Since defects alter the repeating unit cell of SWCNTs, lattice dynamics is unable to produce phonon dispersion of defective SWCNTs similar to the 72 branch phonon dispersion curves of a pristine (6, 6) SWCNT.

In view of this, in the present study, we resort to comparing the density of states (DOS) by noting that the Fourier transform of the autocorrelation function of atomic velocities identifies deviations in normal mode frequencies caused by side-wall defects. Figure 10 shows the phonon density of states of the (6, 6) SWCNTs with 1%, 2%, and 3% vacancy concentrations, prior to (Fig. 10(a)) and following the 3 ns heat treatment procedure (Fig. 10(b)). Most noticeably, vacancies reduce mode degeneracies identified as peaks, especially at frequencies less than 30 THz. Similar reductions in DOS peaks were found in SWCNTs with randomly placed phenyl groups chemically bonded to the tube exterior.31 However, as long as average phonon group velocities remain unaltered, reduced phonon mode degeneracies are unlikely to have a significant effect on thermal conductivity. Figure 10(a) highlights subtle reductions in phonon mode frequencies, which may be the result of reduced phonon group velocities caused by increased structural compliance with vacancy concentrations. Group velocity reductions, especially for phonon frequencies below 10 THz, are understood to be an additional mechanism that may reduce thermal conductivity. Qualitatively, Fig. 10(a) indicates that the frequency and group velocities of phonons are not largely affected by defects. For this reason, reduced phonon relaxation times are likely to be the dominating mechanisms limiting thermal (phonon) transport in SWCNTs with side-wall defects.

Heat treatment produces structures that better retain the phonon DOS peaks for frequencies less than 30 THz (Fig. 10(b)). The DOS peaks of the heat-treated CNTs below 10 THz exhibit a lesser degree of reduction in frequency when compared to the non-heat treated samples (Fig. 10(a)). In addition, the presence of the non-hexagonal side-wall defects have the greatest impact on the optical mode peak near 50 THz, with the 3% vacancy heat-treated samples showing the greatest distortion (spreading) of the 50 THz peak. This broadening of the optical mode was attributed by Padgett and Brenner,31 to the increased number of sp3 bonded carbon atoms due to functionalization of the SWCNT side-walls with the phenyl groups. The introduction of sp3 carbons into the nanotube structure was understood to create defects for phonons to interact and scatter from, thus reducing their mean free path and hence phonon transport. As suggested by the phonon density of states calculation in Fig. 10, it is reasonable to suggest that increased concentration of vacancies does not alter...
Acoustic modes of phonon dispersion, especially at frequencies less than 30 THz, and hence phonon dispersion is not expected to play any significant role in controlling thermal conductivity in SWCNTs in the presence of vacancies or non-hexagonal side wall defects. Therefore, it is reasonable to suggest that thermal conductivity reductions in the presence of vacancies are primarily a result of phonon mean free path interruptions at the non-hexagonal defect sites.

Experimental determination of thermal conductivity in individual MWCNTs

In a recent study,34 the authors reported thermal conductivity measurements in individual MWCNTs in both heat-treated and non-heat treated MWCNT samples using a three-omega based Wollaston T-Type probe inside a high resolution scanning electron microscope (SEM). Details of the determination are as follows:

<table>
<thead>
<tr>
<th>Annealing time</th>
<th>Non heat-treated</th>
<th>3ns</th>
<th>5ns</th>
<th>10ns</th>
<th>22ns</th>
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<tr>
<td>Thermal conductivity in a (6, 6) SWCNT of 10 nm length (W/m-K)</td>
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<td>20.8</td>
<td>20.8</td>
<td>25.6</td>
<td>27.3</td>
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<td>Vacancies</td>
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<td>Mono-vacancy</td>
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<tr>
<td>Di-vacancy</td>
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<td>1</td>
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<td>5 defect</td>
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<tr>
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<td>7</td>
<td>10</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
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<td>25</td>
<td>22</td>
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</table>

FIG. 9. (a) Transformation of side-wall vacancy defects with time in a 10 nm length (6, 6) SWCNT with 3% vacancy concentration at a high temperature heat-treatment of 3273 K. (b) Evolution of thermal conductivity in 10 nm length (6, 6) SWCNT as a function of annealing time at 3273 K.
technique and measurements are provided in Bifano et al.\textsuperscript{34} Two sample groups were investigated: (1) MWCNT samples synthesized via thermal CVD; and (2) MWCNT samples synthesized via thermal CVD and subsequently heat-treated at 3000 °C for 20 h (thermal annealed) in argon. The heat-treated thermal CVD MWCNT samples were acquired from US Nanomaterials Research (US4400, US4406, US4412). The second set of samples, termed “non-heat treated,” comprise of thermal CVD grown MWCNTs purchased from US Nanomaterials Research (US4309, US4315) and NanoLab (PD15L5-20). The NanoLab samples were synthesized at 600 ± 15 °C, and all US Nanomaterials Research samples were CVD grown at 665 ± 15 °C.

Six non heat-treated and 15 heat-treated MWCNTs were measured to determine the effect of high temperature heat treatment on thermal conductivity. Qualitative assessments of residual amorphous carbon and defects were made by observing the Raman peak intensities of the D and G-bands. The D band (defect band) is known to be activated by both carbonaceous impurities with sp$^3$ bonding and fragmented sp$^2$ bonds, both being features of MWCNT defects. The G band is activated by contiguous sp$^2$ bonding, i.e., a high degree of crystallinity. Therefore, when comparing the two sample groups, a smaller D/G band ratio is representative of a sample with fewer number of defects, and hence a higher degree of graphitization. The mean thermal conductivities and Raman D/G ratios of the non-heat treated MWCNT samples provided by US Nanomaterials Research and the non-heat treated MWCNT samples provided by NanoLab are found not to have a statistically significant difference. For this reason, both sample sets were placed into the same non heat-treated sample group.

The non-heat treated samples were found to produce Raman D/G ratios that were approximately 3.3 fold greater than the heat-treated batches indicating a significant presence of average defects and amorphous carbon content. The average Raman D/G ratio for heat-treated samples was 0.21 ± 0.04, while the non-heat treated group had an average D/G ratio equal to 0.69 ± 0.15.

Figure 11 suggests that samples selected from the heat-treated batches produce a mean thermal conductivity nearly 5 fold times (4.88 ×) that of the non-heat treated group (216 ± 149 W/m-K and 44 ± 29 W/m-K, respectively). Note the large standard deviations are due to the variations in thermal conductivity within the group and do not reflect measurement uncertainty. Comparison of the non-heat treated and heat-treated samples using a one-way analysis of variance resulted in a p-value of 0.015 indicating that the graphitization process has a statistically significant effect on the thermal conductivity of the samples. Due to the unique morphology of each sample tested, MWCNT thermal conductivity may be better evaluated on a more sample specific level. Phonon mean free path can be estimated by assuming that the thermal conductivity obeys the bulk expression $k = 1/3 \frac{C}{\nu} \lambda$, where $k$ is the thermal conductivity, $C$ is the specific heat, $\nu$ is the phonon group velocity, and $\lambda$ is the phonon mean free path. Considering a value of the specific heat of graphite at 293 K as 1.63 × 10$^6$ J/m$^3$-K, and a Debye
velocity of approximately $v \approx 1.48 \times 10^4$ m/s, the phonon mean free path of the heat-treated group is approximately equal to 30 nm as compared 5 nm for the non-heat treated group.

**SUMMARY AND CONCLUSIONS**

Classical MD simulations are used to investigate the sensitivity of thermal conductivity to side-wall defects in SWCNTs. A significant finding of this study is that phonon transport in (6, 6) SWCNTs is nearly equally impeded by side wall functionalization when compared to atomic vacancies. The AIREBO interatomic potential predicts that 2 at. % hydrogenation and 1.5%–2% vacancy concentrations have similar detrimental effects. The results suggest that purification measures using liquid or gas phase oxidation that have similar detrimental effects. The numerical calculations of high temperature heat treatment are in qualitative agreement with previously discussed literature on purification schemes and experimental evidence of increases in CNT thermal conductivity with high temperature heat treatment.34 Vacancy repair is evident with heat treatment. Heat treatment of SWCNTs to 3000 °C has the potential to leave covalently bonded functional groups on the CNT side-wall may have a detrimental effect on thermal conductivity. Similarly, residual amorphous carbon on the outer walls of CNTs is also likely to reduce the thermal conductivity.

**ACKNOWLEDGMENTS**

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