IRRADIATION STABILITY OF CARBON NANOTUBES AND RELATED MATERIALS

A Dissertation

by

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ABSTRACT

Application of carbon nanotubes (CNTs) in various fields demands a thorough investigation of their stability under irradiation. Open structure, ability to reorganize and heal defects, and large surface-to-volume ratio of carbon nanotubes affect materials’ radiation response so that it differs from their bulk counterparts. Despite the work conducted to this date, radiation damage and mechanisms governing the evolution of CNTs under irradiation are still deficient in fundamental understanding.

This dissertation is aimed to comprehend and characterize radiation response and crystalline-to-amorphous transition in ion and electron irradiated carbon nanotubes using various techniques, including but not limited to, transmission electron microscopy (TEM) and Raman spectroscopy. It shows that ion irradiation can be used to engineer properties of nanotubes in a controllable manner and significantly improve thermal diffusivity and conductivity of the material. This work also establishes the role of nuclear and electronic stopping powers in thermal diffusivity enhancement: thermal properties of irradiated CNTs are governed by nuclear stopping power of bombarding species. The change of thermal properties with irradiation is driven by two competing mechanisms: inter-tube displacement-mediated phonon transport and defect-induced phonon scattering. In addition to experiments, molecular dynamic simulations are used to confirm validity of the obtained results.

Radiation damage in CNTs at various temperatures as a function of ion energy, flux and fluence is examined. Mechanisms governing crystalline-to-amorphous
transition under electron and ion irradiations are explored, applicability of previously suggested models discussed, and new models introduced. The results show enhanced defect annealing at elevated irradiation temperatures, which delays the formation of amorphous regions. Investigation of nanotube stability after various processing techniques and irradiation indicated that radiation response of CNTs in a composite is similar to that of individual nanotubes.
DEDICATION

To Abibakhan, Kayirzhan, Ashir, and to Dinmukhamed
ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisor and committee chair, Dr. Lin Shao, for his guidance, support, vision, and for giving me the freedom to choose the research topic that I was interested in.

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Finally, I thank my family for the encouragement, support, love, and endless patience. This dissertation could not have been written without them.
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<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AIREBO</td>
<td>Adaptive Intermolecular Reactive Empirical Bond Order</td>
</tr>
<tr>
<td>BC</td>
<td>Boron Carbide</td>
</tr>
<tr>
<td>BWF</td>
<td>Breit-Wigner-Fano</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
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<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>Eq.</td>
<td>Equation</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>DI</td>
<td>De-Ionized</td>
</tr>
<tr>
<td>DP</td>
<td>Diffraction Pattern</td>
</tr>
<tr>
<td>DPA</td>
<td>Displacement per Atom</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>He</td>
<td>Helium</td>
</tr>
<tr>
<td>InSb</td>
<td>Indium-Antimonide</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>kV</td>
<td>Kilo Volt</td>
</tr>
<tr>
<td>LAMMPS</td>
<td>Large-Scale Atomic Molecular Massively Parallel Simulator</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MV</td>
<td>Mega Volt</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>PKA</td>
<td>Primary Knock-On Atom</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dedocyl Sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SRIM</td>
<td>Stopping and Range of Ions in Matter</td>
</tr>
<tr>
<td>SW</td>
<td>Stone-Wales</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TK</td>
<td>Tuinstra and Koenig</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Xe</td>
<td>Xenon</td>
</tr>
<tr>
<td>ZBL</td>
<td>Zieger-Biersack-Littmark</td>
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1. INTRODUCTION AND BACKGROUND

1.1. Introduction

Discovery of carbon nanotubes (CNTs) by Iijima in 1991 uncovered new horizons for researchers around the world.\textsuperscript{1} Theoretical and experimental studies on carbon nanotubes proved that the material has unique thermal, mechanical, optical, and electronic properties.\textsuperscript{1-6} CNTs can be employed in fabrication of nonvolatile memory elements such as molecular micro-switches, advanced sensors and detectors, and shielding materials for neutron sources.\textsuperscript{5-13} Further investigation indicated that materials properties could be modified by ion irradiation.\textsuperscript{5, 14-16} In addition, ion beam was used to change atomic structure and tube morphology, bend, cut, thin, slice CNTs, and interconnect adjacent tubes to form various junctions.\textsuperscript{5, 16-18}

Defect formation, crystalline-to-amorphous transition, and defect agglomeration mechanisms have been extensively studied in graphite, but applicability of the gained knowledge to carbon nanotubes requires careful experimental validation. Despite the effort to comprehend radiation response of the tubes, mechanisms governing evolution of CNTs under irradiation remain poorly understood. The purpose of this dissertation is to shed the light on irradiation effects on CNTs and CNT-containing materials, including defect formation and accumulation mechanisms, crystalline-to-amorphous transition, and many others.
1.2 Structure Of CNTs

Carbon nanotubes can be thought of as rolled-up graphene sheets or hollow cylinders consisting of carbon atoms. When graphene honeycomb lattice is rolled up to form a nanotube, chiral vector becomes a circumference of the tube (see Fig. 1). This chiral vector $C$ uniquely defines each CNT as $(n, m)$ nanotube and is expressed as: $C = na_1 + ma_2$, where $n$ and $m$ are chiral indices, and $a_1$ and $a_2$ are graphite vectors. It plays an important role in determining electronic band structure, spatial symmetry group, and other properties of CNTs.

FIG. 1 Graphene with graphite unit vectors $a_1$ and $a_2$, chiral vector $C$, and chiral vectors for zigzag and armchair nanotubes.
Depending on symmetry with respect to nanotube axis, nanotubes can be categorized as zigzag \((n, 0)\), armchair \((n, n)\) and chiral \((n, m)\). Nanotube diameter can be theoretically calculated by using chiral indices:

\[
d = \frac{a\sqrt{3(n^2+nm+m^2)}}{\pi}
\]  

where \(a\) is the bond length between carbon atoms, known as lattice constant of graphite.\(^3\)

### 1.3 Ion Solid Interactions

#### 1.3.1 Ion Range And Energy Loss

Energetic particles bombarding a material undergo a series of collisions with electrons and lattice atoms, transfer energy to the lattice, create primary knock-on atoms (PKAs), and initiate a displacement cascade. The range of ion in the material depends on the energy loss rate along the ion path:

\[
R = \int_{E_0}^{0} \frac{1}{\frac{dE}{dx}} dE
\]  

where \(E_0\) is the incident energy of the ion and \(dE/dx\) is the energy loss per increment of ion path.\(^1^9\) The penetration depth and energy loss rate are determined by atomic number of ions and a target material, and an ion energy. Distance traveled between collisions and energy loss per collision is random, and depths to which individual ions penetrate are not the same. This range distribution of ions is referred to as straggling. The net penetration depth/projected range \(R_p\) is measured along the direction of incidence and is defined as the total path length of projectile.\(^1^9\) Coulomb interactions of ions with target atoms and
electrons govern energy loss rate, which is subdivided into two mechanisms: electronic and nuclear collisions, and can be expressed as:

\[
\frac{dE}{dx} = \frac{dE}{dx} |_n + \frac{dE}{dx} |_e
\]

where subscripts \( n \) and \( e \) symbolize nuclear and electronic collisions, respectively.\(^{19}\)

Schematic representation of the energy loss mechanisms in a target material can be seen from Fig. 2.
1.3.2 Electronic And Nuclear Stopping Mechanisms

Electronic collisions, in which impinging particles excite or eject electrons of the material, are responsible for insignificant lattice disorder and minor angular deflections of trajectories. Electronic collisions dominate at high energies and low atomic numbers. Nuclear energy loss rate, known as the amount of energy ions lose in elastic collisions per unit length, is of great importance in low energy region. During nuclear collisions energy is transferred to a target atom completely, with large discrete losses of energy, and substantial angular deflections. These collisions can lead to the displacement of atoms from their lattice sites, and consequent formation of lattice disorder.

A comparison between nuclear and electronic energy losses is provided in Fig. 3. Nuclear energy loss dominates when ion velocities $v$ are lower than the velocity of atomic electrons $v_0$, at which ions are neutralized by capturing electrons. Nuclear energy loss decreases as $1/E_0$ with increasing velocity of ions, and electronic energy loss starts to prevail. Electronic energy loss is proportional to $E^{1/2}$ in the range from $0.1v_0$ to $Z_1^{2/3}v_0$, but at $v \geq v_0Z_1^{2/3}$ ion will be stripped of all electrons because the charge state of an ion increases with velocity. Once velocity exceeds the threshold value, ion can be thought of as a positive point charge $Z_1$, with a velocity surpassing the mean orbital velocity of electrons in a target atom.\textsuperscript{19}
FIG. 3 A comparison between nuclear energy loss and electronic energy loss in a material.
1.3.3 Damage Cascade

As it has been mentioned, impinging ion, slowing down in a solid, undergoes collisions with atoms in a lattice. Energetic particles transfer energy to the target material and produce radiation damage. Radiation damage includes the following: interactions between energetic particles and lattice atoms, displacement of lattice atoms by incident particles through kinetic energy transfer, displacement of atoms from their lattice sites by primary knock-on atoms and creation of additional PKAs, all of which results in formation of collision events sequence known as a displacement cascade. Once PKA becomes an interstitial in a lattice site, damage event is treated as complete, and propagation of vacancies, interstitial atoms, and defect clusters around the ion track are considered to be the result of such event. This phenomenon impacts mechanical and physical properties of the material.

In analysis of spatial distribution of point defects, average distance traveled by energetic particle between displacement collisions with target atoms, so called mean free path $\lambda_d$, is one of the most important parameters. Mean free path of an ion slowing down in a target decreases until PKA is produced at every lattice site onward ion path. Once mean free path of an ion reaches an interatomic spacing, high-density cascade in a limited volume, defined as spike, should be taken into account (see Fig. 4). According to the investigation of Brinkman, highly damaged region will be formed when $\lambda_d$ is comparable to atomic spacing of the target atoms. In this damaged region displaced atoms are extruded from the path of incoming ion or PKA, which results in formation of a volume consisting of a shell of interstitial atoms enclosing a core of vacancies. By the end of the
displacement spike, energy of displaced atoms decreases to a point when no further displacements can be tracked. Energy of collisions will be distributed among neighboring atoms and released as lattice vibrations. In the next stage energy is transmitted to surrounding atoms and stable lattice defects are produced, after which mobile defects are able to leave cascade region and create more comprehensive defects.19

FIG. 4 Schematics of a displacement spike.
Displacement of a target atom from its lattice site and subsequent formation of a stable interstitial occurs if an atom receives a minimum amount of energy from an energetic ion in a collision. Energy required to produce a displacement, known as a displacement energy $E_d$, corresponds to the displacement threshold. Depending on the amount of energy transferred to a lattice atom ($T$), following processes can occur: a) if $T < E_d$, target atom will remain at its lattice position but will be subjected to large-amplitude vibrations, which release energy as phonons and appear as a localized source of heat; and b) if $T > E_d$, target atom will be displaced from its lattice site to an interstitial site and a vacancy will form. This vacancy-interstitial defect is known as a Frenkel pair.

Kinchin-Pease model calculates the number of atoms translated by PKA. The model relies on the following assumptions: a) cascade originates from a sequence of two-body elastic collision between atoms; b) probability of displacement is equal to 1 when $T > E_d$; c) positions of atoms in a solid are random; and d) electronic stopping is neglected at energies below the cut-off energy $E_c$. The relationship between the number of displaced atoms and PKA energy, based on Kinchin-Pease model, is provided in Fig. 5. Based on the provided assumptions, Kinchin-Pease model is formulated in the following way:

$$\text{Number of displacements} = \begin{cases} 0 & \text{for } T < E_d \\
1 & \text{for } E_d < T < 2E_d \\
\frac{T}{2E_d} & \text{for } 2E_d < T < E_c \\
\frac{E_c}{2E_d} & \text{for } T \geq E_c \end{cases}$$

(4)
Radiation damage is typically measured in displacements per atom (dpa), which considers that each atom in a volume subjected to irradiation has been translated from its equilibrium position at least once. Displacement per atom at depth $x$ ($dpa(x)$) per unit dose can be estimated by using Kinchin-Pease model based on assumption that number of displacements per unit depth at a depth $x$ ($N_d(x)$) can be expressed as follows:
\[ dpa(x) = \frac{0.4F_D(x)}{NE_d} \varphi \]  

where \( F_D(x) \) is the deposited energy depth distribution function, \( N \) is the number of displacements, \( \varphi \) is an ion dose (ions/cm\(^2\)).\(^{19}\)

### 1.3.4 Irradiation-Induced Defects In CNTs

Experimental observations and theoretical predictions indicate that vacancies and interstitials/adatoms are the most abundant irradiation-induced defects in CNTs.\(^5\), \(^{14,20-22}\) After formation of a vacancy, in attempt to reconstruct the nanotube surface, dangling bonds recombine and create a pentagon. Pentagon can bond with interstitial C atom or can attach to the opposite pentagon with one of its dangling bonds.\(^{20,23}\) This rearrangement of C atoms on the surface, referred to as saturation of energetically unfavorable dangling bonds, initiates localized tube shrinkage. Not only single-vacancies but also multi-vacancies in nanotubes tend to reconstruct by saturation of dangling bonds and local contraction.\(^{20,24}\) Surface reconstruction can be further promoted by Stone-Wales bond rotation.\(^5\) In addition to single- and multi-vacancies and adatoms, irradiation can produce inter-shell covalent bonds and covalent bonds between neighboring nanotubes.\(^{25-26}\) Covalent bonds between adjacent tubes are the result of vacancies or Wigner defects, while inter-shell bonds are formed as a result of two dangling bonds at vacancies in adjoining tubes.\(^5\) The described formation of defects in CNTs was determined predominantly using modeling.
2. MATERIALS AND METHODS

2.1 Sample Fabrication

2.1.1 Chemical Vapor Deposition Of MWNTs

MWNTs of interest were fabricated using chemical vapor deposition (CVD) method. CVD is based on thermal decomposition of hydrocarbon gases in the presence of metal catalyst particles and is one of the most abundantly used methods for large-scale production of CNTs. In this method, catalyst materials are heated to high temperatures (773-1473 K) in a furnace with hydrocarbon vapor flowing for the specified periods of time (15-60 min). CNTs growth involves decomposition of gases, such as acetylene (C$_2$H$_2$), ethylene (C$_2$H$_4$), xylene (C$_8$H$_{10}$) or benzene (C$_6$H$_6$), on catalytic metal (nickel, cobalt and iron). Carbon, required for nanotube growth, is produced as a result of dissociation of the precursor hydrocarbon into the hot catalyst particles. As-dissolved carbon precipitates and crystallizes into energetically stable cylinders after reaching carbon solubility limit in the metal. The process is driven by thermal gradient caused by heat release from exothermic hydrocarbon decomposition and heat absorption from endothermic carbon crystallization. Catalyst size determines whether SWNT or MWNT is formed: larger particle size is expected to produce MWNTs.

CVD offers high yield and purity of specimens, structure and architecture control, variety of forms and alignments, good control of growth parameters, and low cost as compared to other methods, such as arc-discharge and laser-ablation. However, CVD lacks accurate diameter and chirality control during fabrication, adequate manipulation of
the number of walls, ability to produce isolated CNTs, and desired crystallinity. In addition, high temperature growth limits technological applications of thermal CVD and the correlation between catalyst metal and CNTs’ physical, electronic, magnetic and chemical properties still needs to be determined.

2.1.2 Preparation Of Freestanding CNT Mats

In addition to dispersed MWNTs, freestanding carbon nanotube mats were used in experiments. During fabrication of the mats CNTs are purified in hydrochloric acid with small concentration of nitric acid to remove residual catalytic particles, rinsed in DI water, filtered, dried, and milled into powder. The obtained powder is suspended in DI water with surfactants, such as sodium dedocyl sulfate (SDS) and Triton X, sonicated to separate agglomerates and achieve proper dispersion, and injected into dead-end filtration unit. The filtration unit can be either vacuum or liquid pressure based: in vacuum filtration suction on the filtrate side controls filtration and gravity is used to assist in settling of suspension prior to applying vacuum, while in the other method high liquid pressure produced from pumping is applied to achieve passage of suspension through the filter. Nanotubes deposited on filter surface transform into a continuous mat, thickness of which is determined by the concentration and volume of the suspension outgoing filtration. Filtered CNTs are removed from the supporting filter membrane and become a freestanding mat.
2.1.3 Preparation Of CNT-Toughened Boron Carbide

CNT containing composites, such as CNT-toughened boron carbide, were used to determine stability of CNTs as a function of processing techniques. Boron carbide, despite its low specific weight, high elastic modulus and hardness, high neutron absorption cross-section and physical/chemical stability at high temperatures has major drawback: poor ductility.\textsuperscript{30-33} Incorporating CNTs into BC matrix can enhance materials’ mechanical properties, and increase its resistance to thermal shock and crack growth. Fabrication of CNT-reinforced boron carbide composite involved hot pressing a mixture of 3-5 % of CNT and 95-98 % of boron carbide powders at 2273 K under 10 ton load, followed by pressure-less sintering at 2273 K for 2 hours. CNT powder was prepared using CVD method described in Section 2.1.1.

2.2 Ion Beam Irradiation

Various particles, such as neutrons, electrons and ions can be used to study radiation effects in materials. Ion irradiation has been used extensively to determine radiation response of the materials, and to simulate neutron irradiation effects and influence of harsh environments, such as outer space and nuclear reactors. Ion irradiation has several advantages over neutron irradiation experiments: it produces little if any radioactivity, has significantly lower cost, and is time efficient.\textsuperscript{34} Differences between ion and neutron irradiations include penetration depth, damage morphology between species with various masses, transmutation reactions, and control of irradiation conditions.\textsuperscript{34} Understanding basic damage processes in a novel material cannot be achieved without
detailed analysis over different irradiation conditions, which means that ion irradiation has to be used in preliminary studies. Two accelerators, 150 kV terminal voltage linear and 1.7 MV tandem accelerators, were used for ion irradiation of CNT mats.

In an accelerator, ions are produced by supplying a constant stream of gas into ion source, consisting of heated tungsten cathode filament that ejects electrons and a biased anode that supplies energy to electrons and ionizes gas. Size of the induced plasma is controlled by copper wire electromagnet surrounding the source. Ionized gas is extracted through the source aperture by a set of negatively charged electrodes and directed to the acceleration column, in which it attains desired acceleration/voltage. The beam is then focused using electrostatic or magnetic lenses and steered towards target chamber through separator magnet, which separates different species based on their mass. Before implantation, separator magnet is set to deflect the beam off the target to eliminate neutral particles, while sweeping magnet is used to uniformly raster the beam across the target area.

The system is maintained at vacuum at all times (pressure in the ion source is around $3 \times 10^{-6}$ torr, in the beam line around $6 \times 10^{-7}$ torr, and in the target chamber around $2 \times 10^{-7}$ torr) to ensure that the energy of ions in the beam is preserved. Prior to each irradiation implant uniformity was confirmed and specimen was implanted while current of the beam was measured throughout implantation period. The total number of ions implanted per unit area, known as ion fluence in (ions/cm$^2$), and flux in (ions/(cm$^2$-s)) were determined for each implantation. To unify the measure of exposure, fluence was converted to the displacements per atom (dpa) values.
2.3 Characterization Techniques

2.3.1 Transmission Electron Microscopy

Two transmission electron microscopes were used in this study: FEI TECNAI G² F20 ST FE-TEM and JEOL JEM-2010 TEM, one equipped with Gatan CCD camera and the other with ORIUS CCD camera. During examination and irradiation microscopes were operated at accelerating voltage of 200 kV.

In TEM electron beam is transmitted through the specimen such that electrons interact with the specimen as they pass through to produce an image. A stream of electrons is formed in the electron gun by field, Schottky or thermionic emission, and accelerated toward the specimen using a positive electrical potential. Image or diffraction pattern (DP) production require several steps: electron stream is initially confined and focused by set of condenser lenses into a thin, monochromatic beam, which is then focused onto the sample using objective lenses to produce an image/DP, after which image/DP is magnified onto fluorescent screen by projector lenses. Formed image can then be recorded using a digital camera or a photographic film.

Combination of different imaging techniques, diffraction and spectroscopic operations in TEM allows extracting: a) lattice spacing, b) chemical information, c) elemental composition, and d) electron structure of atoms in a specimen that aids in determining bonding/valence state, band gap, and specimen thickness. TEM is important and very useful characterization tool, nevertheless some limitations/challenges associated with it exist. The limitations of TEM include the following: a) it is not designated for sampling, only small regions on the specimen can be observed at one time; b) TEM
micrograph has no depth sensitivity and the data interpretation can be challenging; c) it is based on acceleration of electrons, which implies that specimen can be damaged; d) specimens should be electron transparent, and their thickness should be less than 100 nm; e) aberrations of the objective lens, such as spherical aberrations $C_s$, are difficult to correct.  

2.3.2 Scanning Electron Microscopy

SEM examination was conducted in FEI QUANTA 600 FE-SEM, operated at accelerating voltage of 30 kV. If TEM uses electrons transmitted through the specimen to produce an image, scanning electron microscope (SEM) generates an image using inelastically scattered secondary electrons or elastically scattered backscattered electrons ejected from the specimen. In SEM electrons generated in a thermionic gun, heated to high temperatures by application of a current, pass through a series of condenser lenses for de-magnification and focusing, and through a set of deflection coils that scan the beam in a raster pattern across the specimen.  

Large depth of field attainable in SEM, allows larger regions of the specimen to be in focus at one time. Combination of higher resolutions and better control of magnification, as compared to light microscopes, and ease of use make SEM a valuable piece of equipment employed in research. SEM can be used to examine surface topography, obtain chemical information and elemental composition, determine crystalline phases, plane spacing, angles between plains, symmetry of crystals in elements, crystal orientation, and to identify grain boundaries.
2.3.3 Raman Spectroscopy

Raman spectra were acquired using Horiba Jobin-Yvon LabRam and Witec Alpha SNOM spectrometers. Horiba Jobin-Yvon LabRam Microscope used 17 mW He-Ne laser and a wavelength of 633 nm, while Witec Alpha SNOM used frequency doubled Nd-YAG laser and a wavelength of 532 nm. Raman spectroscopy is a nondestructive light scattering technique that is based on inelastic scattering of monochromatic light from a laser source by atoms or molecules of the material. Interaction of photons of monochromatic frequency in laser light with the specimen results in their absorption and reemission with frequencies shifted up or down from the original value. This so-called Raman effect provides insight to vibrational, rotational and other low-frequency modes in molecules.37

In a Raman system, laser beam in the ultraviolet (UV), near infrared (IR) or visible range is focused through a pinhole onto the filter, reflected to the microscope by optics, and passed into monochromator and detector to create Raman spectrum. A plasma filter removes any background radiation from the laser or emission from lines other than main exciting line of the laser.

Advantages of Raman spectroscopy are numerous: a) it provides both qualitative and quantitative analysis; b) high sensitivity allows distinguishing between molecules of similar chemical origin; c) can be used to characterize solids, liquids, and gases; d) requires little sample preparation if any; e) during analysis specimen can remain in any transparent container, such as glass, polymer, etc., if needed; f) is non-destructive in nature; and g) during analysis specimen and instrument do not contact.37 The drawbacks
associated with this technique include: a) low detection capability because of the weak Raman effect; b) shielding of spectrum due to the presence of fluorescence or specimen impurities; and c) non-applicability to metals or alloys.\textsuperscript{37}

### 2.4 Laser Flash Apparatus

Thermal diffusivity of the specimens was determined using LFA 447 NanoFlash Light system, equipped with Xe flash lamp, operated at the power of less than 10 J/pulse. Laser flash apparatus is based on the use of flash method in which short light pulse is applied to the front side of the material, while the temperature rise on the opposite side of the specimen is measured as a function of time by an infrared detector. High performance xenon flash lamp inside parabolic mirror produces and homogeneously applies the heat pulse to the front of the sample, which can be heated using integrated furnace for temperature-dependent measurements. During the pulse/heating, sample temperature is measured using a sensor integrated into specimen holder plate. Temperature raise is monitored using liquid-nitrogen cooled indium-antimonide (InSb) detector in non-contact manner. The resulting temperature-versus-time curve is then evaluated to determine thermal diffusivity and specific heat of the specimen. Mathematical models in software consider heat conduction problem for the semi-infinite specimen exposed to a flash of energy, as well as compensate for radial/facial heat losses and finite pulse effects.\textsuperscript{38}

Thermal diffusivity of the material is determined using a half-time method: $\alpha=b \times d^2/t_{1/2}$, where $\alpha$ is the diffusivity, $b$ is a constant, $d$ is specimen thickness, and $t_{1/2}$ is the time it takes the rear surface to reach half its maximum temperature.\textsuperscript{38} Specific heat is
determined by a comparative method, which requires identical test conditions for unknown and reference materials, matching specimen dimensions, and equivalent surface structure between sample and reference material. Using evaluated diffusivity and specific heat, thermal conductivity can be estimated for the specimen with known density: 
\[ \kappa = \alpha \times C_p \times \rho, \]
where \( \kappa \) is conductivity, \( C_p \) is specific heat and \( \rho \) is material density.\(^{38}\)

As any other method used in research, laser flash has several restrictions associated with it: a) limited specimen thickness to allow heat pulse to travel through; b) opaqueness of the specimen; c) non-uniform heating; d) finite pulse time effects which can be accounted for using mathematical models; and e) issues associated with accurate determination of specific heat for various materials.\(^{39}\) However, versatility of the method, ability to non-destructively determine diffusivities of the various materials, low cost, high speed, and user-friendly interface compensate for the drawbacks.

2.5 High Temperature Annealing

Various specimens were annealed in vacuum tube furnace after ion irradiation at temperatures ranging from 823 K to 1123 K for 15 min. This high temperature vacuum tube furnace with silicon carbide heating elements fixed below and above the heated chamber was equipped with thermocouple for precise temperature measurements. Temperature uniformity was achieved by using graded layers of insulation and insulation vestibules, while heating was controlled using Lindberg temperature controller. Since cooling depends on heat dissipation and is slow in vacuum, argon purging was used to increase the cooling rate. Specimen was inserted into heating chamber at set temperature
for annealing, extracted after heat treatment for determined period of time and cooled in vacuum. The vacuum pressure was monitored using ionization gauge and its value was better than $2 \times 10^{-7}$ torr.

### 2.6 Molecular Dynamics Simulations

Molecular dynamics (MD) simulation code LAMMPS was used to investigate the mechanisms governing thermal properties of irradiated CNTs. As any MD code, LAMMPS is designed to solve Newton’s equations of motion for a system of particles with known interaction models and boundary conditions. The set of differential Newton’s equations are given by:

$$ m_i \frac{d\vec{\mathbf{v}}_i}{dt} = \sum_j F_2(\vec{\mathbf{r}}_i, \vec{\mathbf{r}}_j) + \sum_j \sum_k F_3(\vec{\mathbf{r}}_i, \vec{\mathbf{r}}_j, \vec{\mathbf{r}}_k) + \cdots $$

$$ \frac{d\vec{\mathbf{r}}_i}{dt} = \vec{\mathbf{v}}_i $$

(6)

where $m_i$ is the mass of atom $i$, $\vec{\mathbf{r}}_i$ is its position vector, $\vec{\mathbf{v}}_i$ is its velocity vector, $t$ is time, $F_2$ is a force function describing interactions between two atoms, and $F_3$ is a function describing three-body interactions. Equation (6) describes evolution of the system with time, which allows empirical characterization of systems’ dynamic behavior without the need to solve Schrödinger’s equation at each time step. To efficiently compute short-range forces for large systems, LAMMPS can use several parallel algorithms, such as atom-, force-, and spatial-decomposition.

Two different potentials were used in this dissertation: adaptive intermolecular reactive empirical bond order (AIREBO) for simulation of radiation damage, and Tersoff
and Zieger-Biersack-Littmark (ZBL) for thermal conductivity simulations.\textsuperscript{40-42} A detailed description of both potentials and further details on LAMMPS code can be found elsewhere.\textsuperscript{40-42}
3. ION BEAM IRRADIATION

3.1 Fluence Effects

Ion beams can be used to investigate radiation tolerance of various materials and manipulate their properties. Radiation response of CNTs, which have large surface-to-volume ratio, open structure, and ability to reorganize and heal defects, differs from their bulk counterparts. Despite the work conducted on carbon-based systems, defect production and crystalline-to-amorphous transformation in CNTs have not been investigated thoroughly. To study radiation tolerance of nanotubes, CNT mats were irradiated with 140 kV He ions at a fixed flux of about $8 \times 10^{12}/(\text{cm}^2\cdot\text{s})$ to fluences ranging from $1 \times 10^{14}$ to $1 \times 10^{16}/\text{cm}^2$. Secondary electron (SE) examination was conducted before and after irradiation to $5 \times 10^{15}/\text{cm}^2$ (Fig. 6), and it did not reveal any noticeable topography changes. After SEM analysis, quantitative characterization of all irradiated specimens was conducted using Raman spectroscopy.

Figure 7 shows Raman spectra of CNTs before and after irradiation with 140 kV He ions to different fluences. Two bands, characteristic to carbon-based materials, were observed at 1340 and 1580 cm$^{-1}$. G band, positioned at 1580 cm$^{-1}$, is assigned to zone center phonons at $E_{2g}$ symmetry.\(^{43}\) It is caused by in-plane bond stretching motion of sp$^2$ C atoms, can form at any sp$^2$ site, and does not require the presence of sixfold rings.\(^{44}\) In defect-free CNTs G band is caused by first-order single resonance process but in defective CNTs it can result from both single and double resonance processes.\(^{44}\) G band broadening with irradiation has been reported in graphite.\(^{45}\) D band, positioned at 1340 cm$^{-1}$, involves
breathing motion of sixfold rings and LO phonons near K zone boundary.\textsuperscript{43, 46-47} Strong dispersion of D band with excitation energy was attributed to Kohn anomaly at K, and its activation to the presence of disorder.\textsuperscript{46-49} D band intensity was determined to be inversely proportional to the dimensions of ordered structure, which implies the increase in D band intensity with increasing radiation damage.\textsuperscript{46-49} Presence of D band in Raman spectrum of unirradiated CNTs indicates the existence of impurities and intrinsic defects, induced by sample fabrication process. As it can be noted from Fig. 7, intensity of D band initially increases with fluence and then begins to decrease. In addition, both G and D modes broaden with increasing radiation damage until they merge at the highest ion fluence of $1 \times 10^{16}$/cm$^2$. Supplementary comparison between Raman spectra of CNTs before and after 140 kV He ion irradiation to fluence of $1 \times 10^{16}$/cm$^2$ is provided in Fig. 8. The insets illustrate the nature of CNT bands: G band arises from the in-plane bond stretching motion of pairs of C atoms and D mode originates from the breathing motion of the sixfold rings. As it can be noted from Fig. 8, both intensity and width of D band increase with irradiation but no position shift is detected. Similarly to SWNTs, G band is split into two modes: G$^-$, related to the in-plane vibration along CNT axis, and G$^+$, associated with in-plane vibration in the direction of the circumference of the tube.\textsuperscript{50} Before irradiation, G$^-$ positioned at 1597 cm$^{-1}$ and a weak G$^+$ at 1615 cm$^{-1}$ were detected and fitted using Lorentzian algorithm. Irradiation transforms G$^-$ and G$^+$ bands into a wider, asymmetric single G mode, which can be described with Breit-Wigner-Fano (BWF) fit (represented by the dotted line in Fig. 8). Unlike D band, position of G band shifts by 10 cm$^{-1}$ from 1597 cm$^{-1}$ to 1587 cm$^{-1}$. At low fluences the peak shift was not identified.
FIG. 6  SE micrographs of CNT mats (a) before and (b) after 140 kV He ion irradiation to the fluence of $5 \times 10^{15}$/cm$^2$. 
FIG. 7 Raman spectra of CNTs as a function of fluence after 140 kV He ion irradiation.
FIG. 8  Raman spectra of CNTs before and after 140 kV He ion irradiation to fluence of $1 \times 10^{16}$/cm$^2$. The dotted line represents BWF fit.
Quantitative characterization of structural defects produced in CNTs was achieved by using the intensity ratio of D to G bands, to be hereafter referred to as \( I_D/I_G \) ratio. Because of disorder-induced origin of D band, its normalization by intrinsic G mode was done for proper characterization of defects in CNTs. Previous experimental results report increase in D band intensity with ion and \( \gamma \) irradiations and its saturation at high fluences, which was attributed to dynamic defect recombination.\(^{51-53}\) However, these reports were based on the assumption of linear proportionality between the number of defects and D mode intensity.\(^{51-52}\) In graphite, deviation from this linear relationship was first observed by Tanabe et al., which implies that linear relationship between \( I_D/I_G \) ratio and disorder should not be assumed, especially at high levels of damage.\(^{54}\)

Full width at half maximum (FWHM) of G band as a function of \( I_D/I_G \) ratio was used to identify the crystalline-to-amorphous transition in 140 kV He ion irradiated CNTs (Fig. 9). As it can be noted from the arrows in Fig. 9, \( I_D/I_G \) ratio increases with increasing ion fluence up to \( 1\times10^{15}/\text{cm}^2 \) and then begins to decrease. The trend change between \( 1\times10^{15} \) and \( 1\times10^{16}/\text{cm}^2 \) corresponds to production of amorphous regions in CNT mats. Similar trend change, when the relationship between FWHM of G mode and \( I_D/I_G \) ratio is reversed, has been reported in graphite.\(^{54-55}\) This observation confirms that \( I_D/I_G \) ratio should not be used to quantify the number of defects in irradiated nanotubes at high damage levels.
Appearance of the maximum in $I_D/I_G$ ratio can be explained using following model: when average distance between individual ion tracks is large (i.e. at low fluence) ion irradiation will increase D band intensity and reduce dimensions of ordered structure without affecting the number of sixfold rings. However, D band intensity will decrease
when long-range order is reduced to the short-range order with increasing number of bombarding ions (i.e. at high fluence). Dimensions of the short-range order are proportional to the size of sixfold rings. In an amorphous state localized existence of short-range order implies continuous breathing motion of sixfold rings when the rings are intact. This means that sixfold rings can persist with increasing ion fluence despite the formation of amorphous regions. It also suggests that the reduction of D band intensity can be used to identify formation of the amorphous regions since long-range order is destroyed before the short-range order.

3.2 Amorphization Model

Discussion provided in Section 3.1 points out that when the damage levels are high, $I_D/I_G$ ratio can no longer be used to quantify the number of defects produced by ion bombardment. Trend, similar to that observed in Fig. 9, can be seen in Fig. 10, which plots normalized $I_D/I_G$ ratio as a function of increasing ion fluence for CNTs irradiated with 140 kV He ions. All $I_D/I_G$ ratios of irradiated nanotubes were normalized by that of unirradiated nanotubes. Normalized $I_D/I_G$ ratio increases with increasing ion fluence up to critical fluence of $5\times10^{15}/\text{cm}^2$, beyond which trend changes and $I_D/I_G$ ratio decreases with further increase in fluence. According to SRIM calculations, the fluence of $5\times10^{15}/\text{cm}^2$ corresponds to 0.15 dpa in the damaged region. Conclusions drawn from Fig. 9 indicate that $5\times10^{15}/\text{cm}^2$ (0.15 dpa) represents the critical ion fluence (dpa) above which structural amorphization is observed. To provide additional proof of the hypothesis, a model describing amorphization in CNTs was developed.
As in CNTs, saturation of $I_D/I_G$ ratio has been observed in graphite with decreasing crystal size.\textsuperscript{43} This trend was previously described by Tuinstra and Koenig (TK), who proposed a theoretical model based on the following assumptions: (a) $I_D/I_G$ ratio reaches a maximum value when the graphite crystal size approaches 2 nm; and (b) maximum $I_D/I_G$ ratio indicates the minimum crystal size for which TK relation is valid.\textsuperscript{43,47} As it has been discussed, ion fluences were sufficiently high to induce an ordered to amorphous transition and deviation from TK relation. Instead of introducing a cutoff fluence for which TK relation is valid, a model with disorder function is proposed to describe Raman response of ion irradiated CNTs and provide a connection to irradiation parameters.

CNTs have a large surface-to-volume ratio, which means that if the amount of free energy exceeds the energy required for amorphization, nanotubes can undergo a crystalline-to-amorphous transition. As a result, long-range order will be destroyed, while short-range order, with a size comparable to the unit cell dimensions, persists. This means that the number of sixfold rings available for D band vibration will be reduced by the destruction of initial order. As it was proposed earlier, even though boundary size effects predicted by TK relation might still have an influence near the critical fluence and beyond, D band intensity will be affected by the reduction of ordered rings. At low fluences the statistical probability of repeatedly damaging disordered rings is negligibly small, while at high fluences it should be taken into consideration. Therefore, the rate change of ordered rings can be described by:

$$dN/dn = -b \times (N_0 - N)/N_0$$

(7)
where $N$ is the number of ordered rings, $N_o$ is the total number of rings in an unirradiated sample, $b$ is the efficiency of creating disordered rings by a single bombarding ion, and $n$ is the ion fluence. The number of ordered rings as a function of fluence is then determined using:

$$N(n) = N_0 \exp(-bn)$$  \hspace{1cm} (8)

A modified TK relation is then expressed as:

$$I_{D/G}(n) = \left[ C(\lambda)/L_a(n) \right] \times \left[ N(n)/N_0 \right]$$  \hspace{1cm} (9)

where $I_{D/G}(n)$ is the $I_D/I_G$ ratio as a function of ion fluence $n$, $C(\lambda)$ is the constant introduced in the TK relation, and $L_a$ is the crystal size, which depends on $n$. The first term $[C(\lambda)/L_a(n)]$ is based on TK relation and the second term $[N(n)/N_0]$ comes from the reduction of ordered rings. The maximum $I_D/I_G$ ratio corresponds to $\frac{N(n)}{N_0} = 0.5$, which can cause an ordered to amorphous transition. In unirradiated CNTs ($n=0$) with no intrinsic defects, crystal dimensions are equivalent to CNT length. However, irradiation-induced defects and damage cascades section a CNT into segments, and the distance between individual defects represents the crystal size:

$$L_a(n) = L/(an + n_0 + 1)$$  \hspace{1cm} (10)

where $L$ is the mean length of a CNT, and $n_0$ is the number of intrinsic defects in a CNT. The efficiency of damage production per ion in a given CNT for a fluence $n$ is described by the parameter $a$, and the cross-section for destruction of sixfold rings can be represented by parameter $b$.

Experimental data was fitted by adjusting parameters $a$ and $b$ in Eqs. (9) and (10), while parameters $C(\lambda)$ and $L$ were eliminated by normalizing $I_D/I_G$ ratio of irradiated
nanotubes to that of unirradiated tubes (Fig. 10). The black and blue dash lines in Fig. 10 correspond, respectively, to two fits taking in consideration only TK relation and only ring destruction. The fit based on TK relation clearly deviates from experimental data and the proposed model above $1 \times 10^{14}/\text{cm}^2$. The proposed model agrees with experimental results reasonably well at $a/(n_0 + 1) = 3.7 \times 10^{-16} \text{ cm}^2$ and $b = 1.3 \times 10^{-16} \text{ cm}^2$. This parameter $b$ should be comparable to the displacement cross-section, which can be estimated using the box-based shape approximation. The average displacement production cross-section was determined to be about $1.1 \times 10^{-16} \text{ cm}^2$, and its value is comparable to the extracted $b$ value.

To confirm validity of the model, TEM examination of the specimens, irradiated to $1 \times 10^{14}$, $1 \times 10^{15}$, $1 \times 10^{16}$, and $5 \times 10^{16}/\text{cm}^2$, was conducted (Fig. 11). After irradiation to fluence of $1 \times 10^{14}/\text{cm}^2$, despite the slight disturbance of basal planes, overall well-ordered structure of the CNTs remains preserved (Fig. 11(a)). Irradiation to $1 \times 10^{14}/\text{cm}^2$ leads to formation of trench-like damage zones across the tubes and further disturbance of basal planes (Fig. 11(b)). Substantial disorder, mixing of basal planes and localized amorphization were observed after irradiation to $1 \times 10^{16}/\text{cm}^2$ (Fig. 11(c)). Structural collapse was noted at $5 \times 10^{16}/\text{cm}^2$, although in some regions ordered structures remained (Fig. 11(d)). TEM results confirm that amorphous regions form after the critical fluence ($5 \times 10^{15}/\text{cm}^2$) is reached.
FIG. 10  

$I_D/I_G$ ratio of 140 kV He ion irradiated CNT mats as a function of increasing ion fluence. The solid lines denote data fitting, based on the model provided in Eq. (9).
FIG. 11  TE micrographs of CNTs irradiated with He ions to: (a) $1 \times 10^{14}$/cm$^2$, (b) $1 \times 10^{15}$/cm$^2$, (c) $1 \times 10^{16}$/cm$^2$, and (d) $5 \times 10^{16}$/cm$^2$. The insets represent corresponding images after Fourier transformation.
3.3 Defect Annealing Effects

Production of defects with irradiation and their dependence on ion fluence has been examined in Sections 3.1 and 3.2. The next logical step was to determine whether irradiation-induced defects could be removed by post-irradiation high temperature treatment. To accomplish that, CNT mats were irradiated with 3 MV H ions to fluence of \(1.7 \times 10^{15}/\text{cm}^2\) and heat treated after irradiation for 15 min at temperatures ranging from 823 to 1098 K. As a result of heat treatment at 1098 K, \(I_D/I_G\) ratio of irradiated specimen decreases from 1.16 to 1.01. The fluence selected for this experiment and its corresponding dpa value do not exceed critical fluence/dpa above which amorphous regions form. This, based on the relationship between \(I_D/I_G\) ratio and radiation damage, indicates that decrease in \(I_D/I_G\) ratio after heat treatment at 1098 K represents efficient defect removal (Fig. 12). By fitting the data with Arrhenius curve (refer to Fig. 12), activation energy for defect removal was extracted to be: 0.36±0.05 eV.

Defect removal with heat treatment was not observed in the specimen irradiated with 140 kV He ions to fluence of \(3 \times 10^{16}/\text{cm}^2\) (Fig. 13). At this fluence radiation damage becomes extensive and amorphous regions form. Produced significant three-dimensional defects, such as cavities surrounded by interstitial atoms and \(sp^3\) clusters, cannot be easily removed. Figure 13 shows increase in \(I_D/I_G\) ratio at the highest temperature of 1123 K, which is consistent with the reported increase in \(I_D/I_G\) ratio at highest annealing temperature in amorphous graphite.\(^{56}\)
FIG. 12  $I_D/I_G$ ratio as a function of annealing temperature for CNTs irradiated with H ions to a fluence of $1.7 \times 10^{15}$/cm$^2$. 

$E=0.36$ eV
The value of extracted activation energy for defect removal is close to migration energy for C atoms (0.5-0.7 eV) in single- and multi-walled carbon nanotubes, which was obtained by atomic scale modeling. These values differ from graphite, in which migration energy of vacancies is ~3 eV and that of interstitials is 0.1 eV. Curvature and one-dimensional structure of nanotubes allows diffusion of carbon atoms as interstitials.
along both outer and inner surfaces of the tubes, since interstitials have lower migration energy than adatoms. However, unknown potential barrier for interstitial-vacancy recombination in CNTs restricts defining the exact physical meaning of the extracted activation energy and further investigation needs to be conducted.

3.4 Irradiation Temperature Effects

To further investigate the defect annealing mechanism in CNTs, specimens were irradiated at room temperature (298 K), 473 K and 673 K, with 140 kV He ion beam to fluences ranging from $1 \times 10^{14}$ to $5 \times 10^{16}$/cm$^2$ at a fixed flux of about $5 \times 10^{12}$/cm$^2$-s. Raman spectra of the specimens were acquired before and after irradiation to $1 \times 10^{16}$/cm$^2$ (Fig. 14). Increase in D band intensity, decrease in G band intensity, and broadening of both bands at all irradiation temperatures can be noted in Fig. 14.

Full width at half maximum of G band as a function of $I_D/I_G$ ratio (Fig. 15) and $I_D/I_G$ ratio as a function of ion fluence (Fig. 16) show a consistently similar trend at all temperatures: initial increase in FWHM and $I_D/I_G$ ratios, followed by a decrease. The maximum in $I_D/I_G$ ratios is observed at $5 \times 10^{15}$/cm$^2$ for irradiations at 298 K (Fig. 16(a)) and 473 K (Fig. 16(b)), and at $1 \times 10^{16}$/cm$^2$ for 673 K (Fig. 16(c)). Following the argumentation provided in Section 3.1, observed $I_D/I_G$ maximum represents the point at which amorphous regions appear. In this case, shift towards higher fluence at 673 K suggests considerable defect annealing and subsequently higher radiation tolerance of CNTs.

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FIG. 14 Raman spectra of unirradiated and 140 kV He ion irradiated (1x10^{16}/cm^{2}) CNTs.
FIG. 15  FWHM of G mode vs. $I_D/I_G$ ratio for CNTs irradiated with 140 kV He ions at (a) 298 K, (b) 473 K, and (c) 673 K.
FIG. 16  $I_D/I_G$ ratio as a function of ion fluence for irradiations at (a) 298 K, (b) 473 K, and (c) 673 K.
In addition to Raman spectroscopy, TEM examination of irradiated specimens was conducted. TEM micrographs of CNTs irradiated to the fluence values of $1 \times 10^{15}/\text{cm}^2$, $5 \times 10^{15}/\text{cm}^2$, $1 \times 10^{16}/\text{cm}^2$ at 298, 473 and 673 K are shown in Fig. 17. The inserts in all micrographs are the corresponding filtered images after Fourier transformation. As it can be seen from the micrographs of CNTs irradiated to $1 \times 10^{15}/\text{cm}^2$ at different temperatures, well-ordered structure with slight disturbance in basal planes is preserved (Fig. 17(a), 17(b), 17(c)). Irradiation to $5 \times 10^{15}/\text{cm}^2$ results in production of trench-like damage zones, dislocation loop-like structures, and mixing and breaking of basal planes (Fig. 17(d), 17(e), 17(f)). In mats irradiated to $1 \times 10^{16}/\text{cm}^2$ at 298 and 473 K, substantial structural collapse and amorphous regions can be seen (Fig. 17(g), 17(h)) but in sample irradiated at 673 K, despite significant structural disorder, amorphous regions are not formed (Fig. 17(i)).

Consistent results provided by both Raman and TEM analyses indicate that amorphous regions form within the fluence region of $5 \times 10^{15}/\text{cm}^2$ to $1 \times 10^{16}/\text{cm}^2$ for 298/473 K irradiations and above $1 \times 10^{16}/\text{cm}^2$ for 673 K irradiation. As it has been shown in Section 3.2, $5 \times 10^{15}/\text{cm}^2 (0.15 \text{ dpa})$ is sufficiently high to damage sixfold rings.

As it can be concluded from the provided results, 298 and 473 K are not high enough to promote efficient defect recombination, which can result in accumulation of defects to immobile clusters. However, at 673 K because of the enhanced mobility of interstitials and vacancies, defects can leave irradiated area and recombine before agglomerating into large clusters. As a result, fluence required to form amorphous regions increases to larger values at elevated irradiation temperatures. These observations and
conclusions are supported by previously reported partial removal of defects in irradiated CNTs annealed ex-situ at temperatures exceeding 573 K.\textsuperscript{14,56,59}

According to theoretical predictions, in CNTs single vacancies become mobile around 1216 K.\textsuperscript{17} Previous studies on graphite indicate removal of unstable in-plane defects, such as single vacancies and vacancy clusters, at temperatures below 573 K.\textsuperscript{60} Recent simulation results show that sputtering of carbon atoms and clustering of adatoms prevents complete removal of defects via interstitial-vacancy recombination mechanism.\textsuperscript{57} Annealing at 673 K has been proven to decrease the number of single- and di-vacancies by \textasciitilde20\%.\textsuperscript{61} These previous studies agree with the results reported in this chapter and indicate that significant defect removal occurs at and above 673 K.
FIG. 17  TE micrographs of CNT mats irradiated with 140 kV He ions to the fluence values of: (a) $1 \times 10^{15}$/cm$^2$ at 298 K, (b) $1 \times 10^{15}$/cm$^2$ at 473 K, (c) $1 \times 10^{15}$/cm$^2$ at 673 K, (d) $5 \times 10^{15}$/cm$^2$ at 298 K, (e) $5 \times 10^{15}$/cm$^2$ at 473 K, (f) $5 \times 10^{15}$/cm$^2$ at 673 K, (g) $1 \times 10^{16}$/cm$^2$ at 298 K, (h) $1 \times 10^{16}$/cm$^2$ at 473 K, (i) $1 \times 10^{16}$/cm$^2$ at 673 K. The filtered images after Fourier transformation are provided in insets.
3.5 Flux Effects

As it has been already shown in Sections 3.1-3.5, critical fluence, above which amorphous regions form, is $5 \times 10^{15}/\text{cm}^2$. Two fluences, one below $(5 \times 10^{14}/\text{cm}^2)$ and the other exceeding $(1 \times 10^{16}/\text{cm}^2)$ critical fluence, were chosen to determine the flux effects on radiation response of CNTs. Two opposite trends were observed: (a) decrease in $I_D/I_G$ ratio with increasing flux in case of lower fluence, and (b) increase in $I_D/I_G$ ratio with ion flux in case of high fluence irradiation (Fig. 18). The trends observed in Fig. 18 indicate that for both fluences damage accumulates at a lower rate at higher than at lower fluxes.

This flux dependence can be explained by beam heating or enhanced interstitial-vacancy recombination. Even though experimental measurements of substrate temperature during high flux irradiation indicated that the temperature rise did not exceed 283 K ($10^\circ$C), damage cascade formation could have promoted localized dynamic annealing of defects. Activation energy for defect removal in CNTs, determined in Section 3.3, is about 0.36±0.05 eV, which implies that defect annealing can be responsible for the observed high flux trend. However, recombination of interstitials from one ion track with vacancies in another ion track, provided that concentration of vacancies is not diluted, could also be responsible for the observed behavior. At low flux, defect recombination efficiency can be reduced by migration of vacancies away from the ion track, which can explain higher accumulation of damage. This model was proposed for hydrogen irradiated Si but it can be applied to CNTs considering usage of light ions for irradiations and that point defects, not large damage cascades, dominate both cases.\textsuperscript{62}
FIG. 18  $I_D/I_G$ ratio as a function of ion flux for CNT mats irradiated with 140 kV He to fluence values of $5 \times 10^{14}$ and $1 \times 10^{16}/\text{cm}^2$.  

$ID/IG$ Ratio

Flux (ions/(cm$^2$-s))

- $5 \times 10^{14}/\text{cm}^2$
- $1 \times 10^{16}/\text{cm}^2$
3.6 CNT-Reinforced Boron Carbide

Because of its unique properties, boron carbide (BC) has been used as neutron absorber in some fission reactors and considered as core component in certain fast breeder reactors.\textsuperscript{33} Despite the advantages of using boron carbide in various fields; its application is limited by poor ductility. Mechanical properties of boron carbide and its resistance to thermal shock and crack growth can be improved by incorporating carbon nanotubes into BC matrix. However, to use CNT-reinforced boron carbide as structural component in fission and fusion reactors, materials’ radiation tolerance needs to be studied. To investigate radiation response of the composite material, specimens were irradiated at room temperature with 140 kV He ion beam to fluences ranging from $1\times10^{14}$ to $1\times10^{17}$/cm$^2$ at a fixed flux of about $6\times10^{12}$/(cm$^2$-$s$). Before irradiation CNT-reinforced BC was inspected in TEM to ensure specimen integrity (Fig. 19). Examination over a large area suggested good adhesion between CNT and ceramic matrix, clustering of CNTs in certain regions, and branching of small CNTs from large nanotubes, presumably caused by sintering process.

Further investigation of the unirradiated composite was conducted using Raman mapping (Fig. 20) over the specimen surface shown in Fig. 20(a), where a white box represents the mapping domain. Non-uniform dispersion of CNTs in the matrix observed in TEM was confirmed by Raman analysis as well. Green, red, and blue colors featured in Fig. 20(b) and 20(c) represent integrated signals corresponding to different Raman bands. Three-dimensional map shown in Fig. 20(c) contains one spectral (intensity of the bands) and two spatial (X and Y coordinates) dimensions.
FIG. 19  TE micrograph of as prepared CNT-toughened boron carbide composite. The white arrow denotes nanotube-matrix interface.

Raman spectra were collected from regions marked as 1, 2, and 3 in Fig. 20(a) to determine how uniform is the distribution of CNTs in a ceramic matrix (Fig. 21). Raman spectrum corresponding to location 1 contains bands positioned at 1346, 1593 and 2664 cm\(^{-1}\), which are characteristic to CNTs. Spectrum acquired in location 2 shows CNTs’ D and G bands superimposed on a broad spectrum with an additional BC peak at 1090 cm\(^{-1}\). Spectrum collected in location 3 contains a BC band at 1090 cm\(^{-1}\) without any distinctive CNT bands. These observations indicate that location 1 corresponds to CNT rich area, location 2 to the boundary between BC and CNT enriched areas, and location 3 to BC matrix.
After the uniformity of the specimens before irradiation was confirmed and CNT enriched regions were identified, composite was irradiated to different ion fluences and Raman spectra corresponding to locations 1 and 3 were collected (Fig. 22). The results show that with increasing ion fluence in CNT enriched areas D mode intensity increases, while both D and G bands broaden and coalesce until two bands merge into one large band at highest fluence of $1\times10^{17}$/cm$^2$. In BC matrix, intensity of the band at 1090 cm$^{-1}$ decreases with increasing fluence, which can indicate partially distorted or amorphous
structure. The nature of the band at 1470 cm\(^{-1}\) is unclear, but it is most likely to be intrinsic to BC and not disorder induced.

To determine CNT stability under irradiation in a host matrix, full width at half maximum of G band was plotted as a function of \(I_D/I_G\) ratio (Fig. 23). The arrows indicate increasing ion fluence. FWHM increases with \(I_D/I_G\) ratio from \(1 \times 10^{14}\) to \(1 \times 10^{16}/\text{cm}^2\), but above this fluence trend changes and increasing FWHM value corresponds to decreasing \(I_D/I_G\) ratio. Similar deviation from the trend was observed when \(I_D/I_G\) ratio was plotted as a function of increasing ion fluence (Fig. 24). \(I_D/I_G\) ratio increased with increasing ion fluence up to \(1 \times 10^{16}/\text{cm}^2\), after which the trend changed and the ratio started to decrease with ion fluence.

The trend change observed in Figures 23 and 24 indicates formation of amorphous zones in CNT enriched regions, which is consisted with previously described amorphization mechanism of CNTs. This suggests that sintering and dispersion of CNTs does not influence their radiation tolerance. In order to use CNT-reinforced composites, such as CNT-toughened BC and many others, radiation-induced degradation of CNTs should be taken into consideration. The effect of radiation damage on mechanical properties of the material should be examined before its application in various fields.
FIG. 21 Raman spectra corresponding to (a) location 1 (CNT enriched), (b) location 2 (boundary between 1 and 3), and (c) location 3 (BC matrix), as denoted in Fig. 20(a).
FIG. 22 Raman spectra as a function of 140 kV He ion fluence in: (a) CNT enriched regions and (b) BC matrix.
FIG. 23  FWHM of G band as a function of $I_D/I_G$ ratio of ion-irradiated composite. The arrows represent increasing ion fluence.
FIG. 24 $I_D/I_G$ as a function of ion fluence for the composite irradiated with 140 kV He.
4. ELECTRON BEAM IRRADIATION

4.1 Diameter Dependent Stability Of CNTs

The mechanisms governing the evolution of multi- and single-walled carbon nanotubes under electron irradiation are still not clear. Because of this, determining amorphization model and diameter-dependent stability of the material is challenging, which limits its application. To understand the crystalline-to-amorphous transition in CNTs, hollow-structured multi-walled carbon nanotubes were irradiated continuously with a 200 kV electron beam in TEM. Electron irradiation was uniform throughout irradiation area without atomic selectivity, and the beam direction was incident to nanotube layers. MWNTs were exposed to an intense focused electron beam to the fluences ranging from $2 \times 10^{23}/\text{cm}^2$ to $2 \times 10^{24}/\text{cm}^2$ at room temperature at a fixed flux.

Three nanotubes with different diameters were selected for the study: hollow carbon nanotube with an initial outer diameter of 11 nm, an inner diameter of 3 nm, and lattice spacing of 3.4 Å, to be hereafter referred to as MWNT-1; CNT with an outer diameter of 22.8 nm, an inner diameter of 6 nm, and lattice spacing of 3.4 Å, referred to as MWNT-2; and a filled nanotube with an outer diameter of 18.4 nm, inner diameter of 5.5 nm, and lattice spacing of 3.7 Å, referred to as MWNT-3.

Figure 25 shows the structural transformation of MWNT-1 under continuous electron irradiation to the fluence of $1.7 \times 10^{24}/\text{cm}^2$. Filtered images after Fourier transformation are provided at the top right corner of each micrograph. As a result of electron bombardment, MWNT structure encountered an ordered-to-disordered transition
and nanotubes’ central hollow was destroyed after 5.8×10^{23}/cm^2 (Fig 25(b)). Non-uniform outer diameter reduction after irradiation to fluences ranging from 1×10^{24}/cm^2 to 1.7×10^{24}/cm^2 (Fig. 25(c)-(d)) was accompanied by lattice spacing increase from 3.4 Å to up to 4.4 Å.

Time-sequential transmission electron micrographs and corresponding Fourier filtered images depicting structural changes in MWNT-2 under electron beam bombardment to 2×10^{24}/cm^2 are provided in Fig. 26. Higher stability of MWNT-2 was noted: despite formation of dislocation loops and reduction in outer diameter after irradiation to 1×10^{24}/cm^2 (Fig. 26(b)), overall ordered structure of the nanotube remains intact. However, after the fluence of 1.5×10^{24}/cm^2 not only outer but also inner shells start moving towards the nanotube center, until the hollow core of the nanotube collapses, and disordering and localized amorphization become significant (Fig. 26(d)). As in case of MWNT-1, irradiation-mediated diameter reduction and lattice spacing expansion in MWNT-2 were not uniform in all regions. Observed structural disintegration of nanotube with irradiation was localized, and beyond bombardment region no significant structural transformations were detected.

It can be argued that beam heating can influence the stability of MWNT-2, due to local increase of target temperature and annealing of radiation damage by surface reconstruction through saturation of dangling bonds and enhanced defect diffusion. However, beam-heating effects are negligibly small because of low inelastic energy loss of electrons and efficient conduction of heat in nanotubes.
FIG. 25  Morphological evolution of MWNT-1: (a) before and after irradiation to (b) $5.8 \times 10^{23}/\text{cm}^2$, (c) $1 \times 10^{24}/\text{cm}^2$, and (d) $1.7 \times 10^{24}/\text{cm}^2$. 
FIG. 26 Structural changes initiated by electron beam in MWNT-2. Corresponding electron fluences: (a) 0 (before irradiation), (b) $1\times10^{24}/\text{cm}^2$, (c) $1.5\times10^{24}/\text{cm}^2$, and (d) $2\times10^{24}/\text{cm}^2$. 
Based on the experimental data, the following is proposed: energetic electrons transfer energy to carbon atoms and displace them from their lattice sites, thus producing vacancies and interstitials/adatoms. Because of nanotubes’ unique morphology, in the presence of a vacancy, two out of three dangling bonds recombine and form a pentagon, which can bond with C adatom or attach to the opposite pentagon with its remaining dangling bond.\textsuperscript{24, 44} As a result, surrounding lattice is pulled inward by neighboring bonds, and, in accordance with mass conservation rules, planes at nanotube ends contract and nanotube diameter/length decrease. Displaced carbon atoms can participate in reconstruction in other portions of the tube, since low activation energy of interstitials (0.4-0.8 eV) allows their migration along outer or inner surfaces of nanotubes and recombination with vacancies.\textsuperscript{59, 63} These atomic rearrangements can be further promoted by the inter-shell covalent bonds that provide additional defect migration path. When the number of defects or deposited energy exceeds a critical value, CNTs can no longer sustain damage and undergo crystalline-to-amorphous transition.

Different stabilities of MWNT-1&2 under electron irradiation indicate that defect production rate and displacement threshold energy for atom removal are diameter dependent. Molecular dynamics simulations were conducted to determine minimum energy required for displacing atoms in CNTs with various diameters.

Minimum displacement energy was calculated for the middle walls in five different MWNTs, each consisting of three walls. Largest MWNT, with an outer diameter of 54.84 Å, consisted of (40, 40), (35, 35), and (30, 30) walls. Other nanotube configurations included: a nanotube with (30, 30), (25, 25), (20, 20) walls and an outer
diameter of \( \hat{A} \), a nanotube with (20, 20), (15, 15), (10, 10) walls and diameter of \( \hat{A} \), a nanotube with (15, 15), (10, 10), (5, 5) walls and a diameter of \( \hat{A} \), and smallest nanotube with (13, 13), (8, 8), (3, 3) walls and an outer diameter of 17.63 \( \hat{A} \). The results indicate that nanotubes with smaller diameter have lower displacement energy as compared to nanotubes with larger diameter (Fig. 27), which can explain lower stability of smaller nanotubes.

![Graph showing minimum displacement energy as a function of nanotube diameter.](image)

**FIG. 27** Minimum displacement energy as a function of nanotube diameter.
Experimental observations also suggest higher rate of atomic displacements in smaller nanotubes (MWNT-1&2) because of the curvature-induced strain in carbon network. The curvature promotes surface reconstruction and decreases minimum energy required to form vacancies: the smaller nanotube diameter/larger curvature, the lower the amorphization threshold. Observed collapse of inner walls in MWNTs can be attributed to the lower stability of inner shells, caused by higher curvature, in combination with higher defect creation rate and migration of interstitials through inner hollow in axial direction.  

Figure 28 shows micrographs and images after Fourier transformation of MWNT-3, filled with transition metal Fe, under continuous irradiation to the fluence of $2 \times 10^{23}/\text{cm}^2$. Basal plane disturbance of innermost walls and inter-shell covalent bonds in outermost walls are observed after $1 \times 10^{23}/\text{cm}^2$ (Fig. 28(b)). With increasing irradiation time d spacing of the tube increases non-uniformly, dislocation loops and additional inter-wall covalent bonds form. After the fluence of $2 \times 10^{23}/\text{cm}^2$ significant disordering and distortion of walls were observed but complete collapse of the tube was not (Fig. 28(d)). Unlike in MWNT-1-2, both inner and outer diameters of MWNT-3 increase upon irradiation thus indicating different radiation response. Opposed to the previously reported results on structural evolution of nanotube filled with iron under electron beam\textsuperscript{11}, this experiment did not result in tube breakage, deformation of the crystal, its extrusion or transformation to nano-cluster from substantial pressure buildup inside of the tube. Atomic simulations predict the pressure buildup to originate from nanotube contraction due to reconstruction of the carbon network.\textsuperscript{11}
FIG. 28  Micrographs of CNTs (a) before, and after irradiation to electron fluences of (b) $1\times10^{23}/\text{cm}^2$, (c) $1.7\times10^{23}/\text{cm}^2$, (d) $2\times10^{23}/\text{cm}^2$. 
It can be argued that since cylindrical shape of all investigated tubes is preserved even upon significant disorder and amorphization, another mechanism besides vacancy based mass reduction, saturation of dangling bonds and inter-tube covalent bonds-based healing must be involved. Recent study indicated that carbon atoms are most likely to abandon the structure through 5|7 defects, which can be thought of as a core of an edge dislocation, rather than through expansion of vacancy clusters. Dislocation core can absorb vacancies/interstitials and thereby reduce total energy, which is associated with stepwise positional movement of 5|7 defect in accordance with atomic loss/accumulation. During this pseudo-climb 5|7 core changes position along the tube length and ejects two carbon atoms at a time, initiating mass reduction. The diameter dependent stability of nanotubes, materials’ amorphization mechanism, and corresponding amorphization threshold values should be considered before potentially using CNTs in various devices.

4.2 Lattice Spacing Change With Irradiation

As it has been mentioned in Section 4.1, lattice spacing in all MWNT increased with irradiation. It should be noted that the lattice spacing increase was not uniform in all regions, wall separation distance ranged from 3.8 to 4.4 Å in hollow structured MWNT-1&2, and from 3.8 to 4.6 Å in a filled MWNT-3. Figure 29 shows that the lattice spacing increase before ordered-to-amorphous transition is more pronounced between two outermost walls (denoted as outer), and is less significant between innermost walls (labeled inner).
FIG. 29  Lattice spacing as a function of electron fluence before ordered-to-amorphous transition in (a) MWNT-1 and (b) MWNT-2.
Observed expansion of lattice spacing upon irradiation can be attributed to spatially isotropic Coulomb explosion, defined by Rayleigh charge instability. During irradiation charged electrons transfer and increase the net charge of the system, which results in accumulation of repulsive electrostatic energy. At Rayleigh instability limit, van der Waals force and Coulomb repulsion are balanced, but with increasing charge Coulomb repulsive force exceeds van der Waals force binding adjacent walls of MWNT and lattice spacing expands to regain charge stability. Curvature-induced strain in smaller diameter nanotubes also facilitates charging of defects introduced by electron beam and promotes Coulomb repulsion between the walls, thus further increasing lattice spacing.
5. THERMAL PROPERTIES OF CARBON NANOTUBES

5.1 Ion Fluence Effects

Irradiation-induced degradation of CNTs and CNT-containing composites has been examined in Sections 3-4, and the focus of this chapter will be radiation-mediated changes of thermal properties. Strong sp\(^2\) bonding of carbon nanotubes suggests phonon-mediated heat transfer, with negligible contribution from electrons. As it has been discussed, displacements and electron excitations are produced in materials by nuclei-nuclei scattering and nuclei-electron interaction during irradiation. Defects are expected to deteriorate thermal properties of the material by scattering phonons and, therefore, by decreasing their mean free path. Most abundant defects in CNTs, namely, mono-vacancies, di-vacancies and Stone-Wales, more effectively scatter intermediate and high frequency phonons than low frequency phonons.\(^{67}\) Recent modeling results indicate reduction by an order of magnitude in thermal conductivity of carbon nanotubes, caused by a small number of defects.\(^{67}\) Large variation in experimentally measured thermal conductivities of individual CNTs, ranging from 300 to 7000 Wm\(^{-1}\)K\(^{-1}\), could be attributed to phonon-defect scattering.\(^{67-71}\) Thermal properties of CNT mats have not been as examined as that of individual CNTs in part because of the more complex phonon transport, including transport across the tubes. To investigate alteration of nanotubes’ thermal properties, CNT mats were irradiated with 3 MV hydrogen ions to fluences ranging from 1\(\times\)10\(^{15}\) to 6\(\times\)10\(^{15}\)/cm\(^2\). The fluence/dpa values were chosen to be below amorphization threshold values of 0.15 dpa to ensure preservation of the initial order.
FIG. 30  Thermal diffusivities of CNT mats before and after irradiation with 3 MV H ions to fluences up to 6×10^{15}/cm^{2}.
Thermal diffusivities of unirradiated and irradiated mats, plotted as a function of temperature, are provided in Fig. 30. As it can be noted from the plot, diffusivity of the mats at 300 K increases from about $1 \times 10^{-7} \text{ m}^2/\text{s}$ (before irradiation) to $3.8 \times 10^{-7} \text{ m}^2/\text{s}$ after irradiation to $3 \times 10^{15}/\text{cm}^2$. To make the trend more obvious, thermal diffusivities of CNTs
at 300 K are plotted as a function of ion fluence (Fig. 31). Increasing ion fluence leads to increase in thermal diffusivities of the mats up to the fluence of $3 \times 10^{15}/\text{cm}^2$, beyond which further enhancement of ion fluence leads to reduction in thermal diffusivity values. At the highest fluence of $6 \times 10^{15}/\text{cm}^2$ thermal diffusivity of irradiated mat abates to $9 \times 10^{-8}$ m$^2$/s, i.e. below the value obtained for an unirradiated mat.

Modeling was used to understand what governs the diffusivity enhancement with irradiation. In the modeling step interactions between tubes within CNT mats were represented by two 20 nm long adjacent MWNTs positioned 3.4 Å apart with 10 nm overlapping, as shown in Fig. 32. Separation distance between the adjacent tubes was selected based on high-resolution transmission electron microscopy examination of nanotubes. Each nanotube was selected to have three walls and an inner diameter of 1.63 nm. Simulation of irradiation damage in nanotubes was conducted using 500 eV C ions, after which Müller-Plathe method was used to produce a heat flux. Before the ion bombardment system was relaxed for 100 ps at 100 K. Interaction and recombination of defects were modeled for up to 2.5 ps, to ensure saturation of defects in a relaxed structure. Simulation results, including positions of atoms and defects, were used as an input to thermal conductivity modeling.

Müller-Plathe method has several advantages, including conservation of both kinetic energy and linear momentum and precise knowledge of the imposed heat flux. In this method, one side of the nanotube is defined as “hot” and velocity vector of atom with highest kinetic energy from “cold” end is exchanged with that of an atom with the lowest kinetic energy from “hot” side. This exchange results in an energy flux in a direction from
“cold” towards “hot” sections of the nanotube and in a temperature gradient in the opposite direction. The energy exchange is repeated periodically every 0.005 ps until thermal conductivity converges with simulation time. Thermal conductivities can be calculated using heat flux and temperature gradient: \( \dot{J} = -\kappa \nabla T \), where \( \dot{J} \) is the heat flux transferred per unit area and \( \kappa \) is the thermal conductivity. Convergence of conductivity with time represents the balance between energy transfer and temperature gradient-induced heat flux. Conductivity value can be determined using following equation:

\[
\kappa = -\frac{\sum_{\text{transfers}} \frac{m}{2} (v_h^2 - v_c^2)}{t A (\partial T / \partial z)}
\]  

(11)

where \( v_h \) and \( v_c \) are velocities of carbon atoms at the “hot” and “cold” sides, respectively, \( m \) is atomic mass of carbon, \( t \) is simulation time, \( A \) is the nanotube cross-section, \( T \) is temperature, and \( z \) is the distance between two ends. By dividing nanotubes into 3 nm thick sections, instantaneous temperatures of “hot” and “cold” sections can be obtained using following expression:

\[
T = \frac{1}{3n k_B} \sum m_i \nu_i^2
\]  

(12)

where the sum is taken over the section with a total of \( n \) atoms, \( m_i \) is the atomic mass of carbon, \( \nu_i \) is the velocity of C atoms, and \( k_B \) is the Boltzmann’s constant.

Change of calculated conductivities with increasing number of bombarding ions is plotted in Fig. 32. Increasing number of defects enhances phonon scattering and subsequently decreases thermal conductivity of an individual nanotube. However, thermal conductivity increase, followed by a decrease as larger number of defects is introduced, was observed in two adjacent CNTs. In these adjacent irradiated nanotubes displaced C
atoms form inter-tube covalent bonds, which promote tube-to-tube phonon transport. Modeling results show that even an individual inter-tube carbon covalent bond can significantly enhance phonon transport across the tubes (Fig. 32). At low ion fluences/levels of radiation damage this inter-tube covalent bond-induced phonon transport compensates for phonon scattering from defects and increases conductivity of nanotubes. As it can be seen from the plot (Fig. 32), calculated conductivity saturates and decreases after reaching critical amount of radiation damage. This indicates that beyond the critical value defect-induced phonon transport presides over inter-tube transport, and that any subsequent increase of defects will further reduce conductivity of CNTs.

Changes in thermal conductivities of irradiated and unirradiated CNTs as a function of simulation time are given in Fig. 33. As it can be seen, curves, depicting unirradiated nanotube and nanotubes bombarded with 33 and 133 ions, decrease with prolonged simulation time without any significant fluctuations. Conductivity of irradiated nanotubes saturates after about 40 ps, while saturation in unirradiated nanotubes is delayed. Conductivity values at 70 ps were selected in calculations since this simulation time is sufficiently long to obtain converged values.
FIG. 32  Calculated thermal conductivities (MD) of an individual MWNT and two adjacent MWNTs as function of number of bombarding ions.
FIG. 33 Calculated thermal conductivities of MWNTs as a function of simulation time.
Figure 34 provides visualization of the heat distribution in two adjacent nanotubes before and after irradiation. A 5 nm thick section of one the left side of the bottom nanotube was heated to 300 K, the rest of the tube and a second nanotube were maintained at 0 K, and distribution of kinetic energies was monitored. Kinetic energy distribution after 0 ps, 0.7 ps, and 3.6 ps in unirradiated and irradiated MWNTs is provided in Fig. 34. As it can be seen from the figure, prior to ion bombardment heating of one nanotube end (to 300 K) results in uniform temperature distribution throughout the nanotube and its energetic vibration without any noticeable effect on the adjacent
nanotube. This lack of influence on the adjacent MWNT can be explained by inefficient phonon transport between two tubes. Ion irradiation introduces defects and gives rise to phonon-defect scattering, which results in buildup of temperature gradient and reduction of temperature on the opposite site of the heated nanotube end. At the same time, irradiation-induced inter-tube displacements promote phonon transport and enhance heat transfer across the tubes, which can be seen from the temperature increase in the adjacent tube. Inter-wall displacements and inter-tube displacements introduced by bombardment with 33 ions are shown in Fig. 34 in blue and red, respectively. This confirms the importance of inter-tube covalent bonds in thermal transport of irradiated CNTs.

Heat treatment of 3 MV H irradiated mat at 1173 K for 15 min resulted in additional thermal diffusivity enhancement from $2.2 \times 10^{-7} \text{ m}^2/\text{s}$ to $2.9 \times 10^{-7} \text{ m}^2/\text{s}$ (Fig. 35). Upon annealing, defect removal reduces phonon scattering and enhances thermal transport within nanotubes. Experimental results provided in Sections 3.3 and 3.4 indicate that low activation energy allows removal of point defects upon heat treatment of CNTs for short periods of time. Elimination of inter-tube covalent bonds, which promote phonon transport in irradiated nanotubes, should decrease thermal diffusivity of the mats. However, carbon adatoms confined by two adjacent tubes are less mobile, and their removal will require much higher activation energy. The combination of reduced phonon-defect scattering and efficient phonon transport across the tubes results in net gain of thermal transport and further diffusivity enhancement.
FIG. 35 Thermal diffusivities of unirradiated and irradiated CNT mats as a function of temperature before and after annealing at 1173 K for 15 min.

Heat treatment of unirradiated mat at 1173 K for 15 min did not initiate significant thermal diffusivity changes (Fig 35). This indicates that diffusivity enhancement observed during heat treatment of an irradiated mat can be attributed to annealing of irradiation-induced defects, which underlines advantages of ion irradiation-assisted phonon
engineering. This also suggests that high temperature treatment alone cannot achieve the results similar to those obtained using irradiation. In other words, phonon transport can be controlled with ion irradiation, and CNT mats can be used in harsh environments with high temperatures.

5.2 Ion Energy Effects

Further investigation of changes in thermal properties of CNTs with irradiation was done by irradiating mats with 1.5, 2, and 3 MV hydrogen ions to fluences ranging from $2 \times 10^{14}$ to $6 \times 10^{15}$/cm$^2$. To ensure preservation of the initial order in CNTs, irradiation fluence/dpa values were selected not to exceed amorphization threshold value of 0.15 dpa. CNTs were examined in SEM before and after irradiation to 1.5, 2, and 3 MV H ions to their respective highest ion fluences (Fig. 36). Secondary electron (SE) micrographs indicate preservation of structural integrity at all irradiation conditions and no apparent densification of the mats. Thickness measurements before and after irradiation confirm that ion bombardment does not initiate any changes in mat thickness. Combination of thickness measurements and SEM examination proved that enhancement of thermal diffusivities of nanotubes with irradiation are not initiated by densification-induced thickness variation.
FIG. 36 SE micrographs of CNT mats: (a) before, and after irradiation with: (b) 1.5 MV H ions to $3.5 \times 10^{15}$/cm$^2$, (c) 2 MV H ions to $4.5 \times 10^{15}$/cm$^2$, (d) 3 MV H ions to $6 \times 10^{15}$/cm$^2$. 
FIG. 37 Transmission electron micrographs of CNT mats: (a) before and after irradiation with: (b) 1.5 MV H ions to $3.5 \times 10^{15}$/cm$^2$, (c) 2 MV H ions to $4.5 \times 10^{15}$/cm$^2$, (d) 3 MV H ions to $6 \times 10^{15}$/cm$^2$. 
FIG. 38 Thermal diffusivities of CNT mats before and after irradiation with: (a) 1.5 MV H ions to fluences ranging from $2 \times 10^{14}/cm^2$ to $3.5 \times 10^{15}/cm^2$, (b) 2 MV H ions to fluences ranging from $2 \times 10^{14}/cm^2$ to $4.5 \times 10^{15}/cm^2$, and (c) 3 MV H ions to fluences ranging from $1 \times 10^{15}/cm^2$ to $6 \times 10^{15}/cm^2$, as a function of temperature.
In addition to SEM investigation, CNTs were analyzed in TEM before and after irradiation to ensure structural integrity of nanotubes after ion bombardment. Transmission electron (TE) micrographs of nanotubes irradiated to highest fluences and their corresponding filtered images after Fourier transformation are provided in Fig. 37.

FIG. 39 Specific heat of graphite as a function of temperature, adapted from Ref. 73.
TEM examination of the specimens revealed preservation of well-ordered structure and overall crystalline quality of irradiated MWNTs. No significant distortion and amorphous zones were detected.

Thermal diffusivities of unirradiated and mats, irradiated with H ions of different energies, are plotted as a function of temperature in Fig. 38. As it can be seen from the figure, thermal diffusivities of the mats increase with ion fluence, with a maximum enhancement from $1 \times 10^{-7}$ m$^2$/s (before irradiation) to $5.4 \times 10^{-7}$ m$^2$/s at 300 K, observed after irradiation to $1.4 \times 10^{15}$/cm$^2$ with 1.5 MV H ions. Similarly to 3 MV H ion irradiation, thermal diffusivities of CNT mats increase with ion fluence at all three irradiation conditions until a critical fluence is reached, after which diffusivities descend with the amount of introduced radiation damage. This suggests existence of a fluence range, in which diffusivity values can be enhanced most.

Experimentally determined thermal diffusivities of CNT mats can be converted to thermal conductivity values using previously reported heat capacity data for graphite, which was proven to agree with heat capacity of nanotubes. Convergence of specific heat curves for graphite, graphene, and multi- and single-walled nanotubes at temperatures above 100 K allows using specific heat of graphite to determine thermal conductivities of CNT mats between 300 K and 450 K. Temperature dependence of heat capacity of graphite, adopted from reference 73, is shown in Fig. 39. As it can be noted from the figure, measured specific heat increases continuously with temperature.
FIG. 40  Temperature dependence of extracted thermal conductivities of CNT mats before and after ion irradiation with (a) 1.5 MV H, (b) 2 MV H, and (c) 3 MV H ions to various fluences.
Extracted thermal conductivities of CNT mats before and after irradiation with 1.5, 2, and 3 MV H ions to different ion fluences are provided as a function temperature in Fig. 40. Weak temperature dependence of extracted conductivities, namely continuous increase with temperature, can be seen. The increase of CNTs’ conductivity with
temperature in low temperature regime (up to 300 K) and decrease with temperature at higher temperatures (> 300 K) was previously attributed to phonon-defect and Umklapp phonon-phonon scattering, respectively.\textsuperscript{75-77} Weak temperature dependence of thermal conductivities (see Fig. 40) suggests that the transition from phonon-defect to phonon-phonon scattering in CNT mats occurs at temperatures exceeding 450 K. For comparison, in isolated single- and multi-walled carbon nanotubes this transition occurs between 100 K and 150 K.\textsuperscript{74, 78} Similar delay from phonon-defect to phonon-phonon scattering has been observed in nanotubes with X and Y junctions, mats and in MWNT bulk materials.\textsuperscript{75-77} Thermal conductivity of isolated nanotubes is orders of magnitude larger than the conductivity of CNT mats, which could be attributed to tube-tube interactions, defects and shorter mean free path of phonons in networked nanotubes. This confirms a more complex phonon transport in CNT mats as compared to individual nanotubes.

Based on the experimental data, it can be concluded that thermal properties of CNTs under irradiation are governed by the displacements produced from nuclei-nuclei scattering or, in other words, by nuclear stopping power of H ions. SRIM calculations indicate that nuclear stopping of H ions in carbon nanotubes depends on energy: $5.3 \times 10^4$ eV/cm (1.5 MV H), $4.1 \times 10^4$ eV/cm (2 MV H), and $3.0 \times 10^4$ eV/cm (3 MV H), and that the maximum of nuclear stopping power is attained around 200 eV.\textsuperscript{42} Therefore, ion fluence values, at which maximum diffusivities of irradiated nanotubes are obtained, increase with increasing ion energy. Normalization of ion fluences by multiplying to corresponding nuclear stopping power values suggests a consistent dependence between
displacements and thermal diffusivity changes at 300 K for all irradiation energies (Fig. 41).

5.3 Ion Projected Range Effects

As it has been postulated in Section 5.2, nuclear stopping power dominates thermal properties of irradiated CNTs. An experiment was designed to confirm the validity of the argument, in which three 100 μm thick CNT mats were positioned on top of one another to form a 300 μm thick target. This assembly was irradiated with 3 MV H ions to fluence of 5×10^{15}/cm². Ions will penetrate through all three mats without doping specimens, because penetration depth of H ions in CNT mats is around 335 μm. Temperature dependence of measured thermal diffusivities of CNTs is provided in Fig. 42. As it can be noted, thermal diffusivities of CNT mats increase from 1×10^{-7} m²/s (before irradiation) to 2.5×10^{-7} m²/s with irradiation (Fig. 42-43).

In this experiment, depth dependence of thermal diffusivity was determined by measuring thermal diffusivities of individual mats. As it has already been discussed, nuclear stopping power is energy dependent, which implies increase in number of displacements, produced in a material with ion penetration depth. By plotting experimentally determined diffusivity values and nuclear stopping of H ions as function of ion penetration depth (Fig. 43), one could clearly see that the maximum enhancement of diffusivity at 300 K was observed in a mat corresponding to ion penetration depth of 100-200 μm. The observed significant diffusivity increase results from increasing nuclear stopping power. Even though diffusivity of the third mat, corresponding to penetration
depth of 200-300 µm, exceeds the value for the unirradiated mat, its value is less than that observed in the top mats. The nuclear stopping power reaches its maximum in the third mat, which would suggest further diffusivity increase. However, increased displacement production at the end of range of H ions leads to extended radiation damage and reduction of diffusivity in the third mat. This confirms the existence of a damage range in which diffusivity of CNTs can be enhanced most.
FIG. 42 Thermal diffusivities of CNT mats before and after irradiation with 3 MV H ions to fluence of $5 \times 10^{15}$/cm$^2$, as a function of temperature.
FIG. 43  Nuclear stopping power and thermal diffusivities of mats before and after irradiation with 3 MV H ions to fluence of $5 \times 10^{15}$/cm$^2$, as a function of ion penetration depth.
6. SUMMARY

In this work stability of individual carbon nanotubes, CNT network, and CNT-containing composites under various irradiation conditions was examined, and the effects of ion energy, fluence, flux, and temperature on materials’ radiation tolerance was determined. Raman spectroscopy, in combination with transmission electron microscopy, was used to identify an ordered-to-amorphous transition in ion beam irradiated CNT mats. An incorrect assumption of linear proportionality between Raman based $I_D/I_G$ ratio and the number of defects/disorder was discussed and a new model, describing the appearance of a maximum in $I_D/I_G$ ratio, was proposed. The proposed model considers change of crystal size and reduction in the number of ordered rings, both of which occur with irradiation.

The onset of an ordered-to-amorphous transition was determined to be around 0.15 dpa at 298 K. However, production of amorphous regions can be delayed by enhanced defect annealing when irradiation temperatures exceed 673 K. This is supported by low activation energy for defect removal (0.36 eV), which was determined using post-irradiation heat treatment of irradiated CNT mats. Radiation response of CNT-reinforced composites was investigated and the results indicate that the threshold fluence/dpa value for an ordered-to-amorphous transition in composite materials is similar to that of CNTs. This suggests that processing techniques, such as sintering, dispersion, and hot pressing, do not affect radiation tolerance of the material.
Electron irradiation of individual MWNTs revealed that an ordered-to-amorphous transition occurs when the number of defects/deposited energy exceeds a critical value. It also showed the diameter dependence of defect production rate and displacement threshold energy, and different stabilities of nanotube walls. Superior properties of CNTs are expected to degrade with crystalline-to-amorphous transition. Therefore, irradiation-induced degradation of nanotubes and CNT-based materials should be taken into consideration for their potential application in various fields.

In addition to initiating irradiation-induced degradation of CNTs, ion beams can be used to engineer properties of the material in a controllable manner. In this dissertation ion irradiation was used to significantly improve thermal properties of networked CNTs. Irradiation-induced defects are known to degrade thermal properties of CNTs by scattering phonons. However, irradiation introduces inter-tube displacements, which provide stable point contacts between adjacent nanotubes and improve phonon transport across nanotube network. Competition between these two mechanisms determines thermal properties of the material. Experimental results in conjunction with modeling proved that thermal conductivity of CNTs continuously increases with irradiation when inter-tube displacement-mediated phonon transport exceeds phonon-defect scattering. Further conductivity enhancement can be achieved by post-irradiation heat treatment, which removes phonon scattering defects without affecting thermally stable inter-tube displacements. In a separate experiment maximum conductivity enhancement was achieved when nuclear stopping power prevailed electronic stopping power of bombarding ions.
To conclude, ion and electron beams can be used to tailor structure and properties of carbon nanotubes. The extent of radiation damage in CNTs and CNT-containing materials was examined and the threshold for crystalline-to-amorphous transition was determined. This work delineates advantages of using ion irradiation to engineer thermal properties of CNTs by controlling irradiation conditions. The results provided in this dissertation describe radiation response of carbon-based nanomaterials, which should be taken into account for their future applications.
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