## EFFECTIVE MECHANICAL PROPERTIES IN CARBON NANOTUBE-SILICA NANOCOMPOSITE

by

Tengyuan Hao

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

Spring 2018

© 2018 Tengyuan Hao All Rights Reserved

## EFFECTIVE MECHANICAL PROPERTIES IN CARBON NANOTUBE-SILICA NANOCOMPOSITE

by

Tengyuan Hao

Approved: \_\_\_\_\_

M. Zubaer Hossain, Ph.D. Professor in charge of thesis on behalf of the Advisory Committee

Approved: \_\_\_\_\_

Ajay K. Prasad, Ph.D. Chair of the Department of Mechanical Engineering

Approved: \_\_\_\_\_

Babatunde A. Ogunnaike, Ph.D. Dean of the College of Engineering

Approved: \_\_\_\_\_

Ann L. Ardis, Ph.D. Senior Vice Provost for Graduate and Professional Education

#### ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Zubaer Hossain, for the continuous support of my Master study and related research, for his patience, motivation, and immense knowledge. The door to Prof. Hossain office was always open whenever I ran into a trouble or had a question about my research. I would never have been able to finish my thesis without the guidance of my advisor Dr. Zubaer Hossain. Thank you for all the support.

I would like to thank my research group, especially Venkateswaran Santhanam, Fazle Elahi and Tousif Ahmed, for always willing to help and give me good suggestions.

Finally, I would like to thank my parents. They were always there supporting me through my years of study in the U.S.

### TABLE OF CONTENTS

LI LI A]	ST ( ST ( BST]	OF TA OF FIC RACT	BLES	viii ix xxi
Cl	hapte	er		
1	INT	RODU	UCTION	1
	1.1	Compo	osite Material	1
		1.1.1	Nanocomposite	4
		$1.1.2 \\ 1.1.3$	CNT-SiO <sub>2</sub> Nanocomposite	7 13
	1.2	LAMN	APS	15
		1.2.1	fix box/relax command	15
		1.2.2	fix npt command	15
		1.2.3	fix nvt command	16
		$1.2.4 \\ 1.2.5$	fix nve command	$\frac{16}{16}$
	1.3	Interat	tomic Potential	17
		1.3.1	Tersoff Interatomic Potential	17
		1.3.2	The Reactive Force-field (ReaxFF) Interatomic Potential $\ .$ .	19
		1.3.3	The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) Potential	21

2	DE AM	FORMA'	TION AND FRACTURE MECHANICS OF OUS SILICON DIOXIDE (GLASS)	23
	2.1	A Metho	od to Create an Amorphous Silicon Dioxide System	24
		2.1.1 A	A Method to Create a Single-crystalline Silicon Dioxide Unit	24
		2.1.2 T	The Thermal Annealing Method to Create an Amorphous Filicon Dioxide System (Tersoff Potential)	24
		2.1.3 T S	The Thermal Annealing Method to Create an Amorphous The Dioxide System (ReaxFF Potential)	29
	2.2	Applying Structur	g Uni-axial Tension Test to the Amorphous Silicon Dioxide	33
	2.3	The Effe Time-ste Rate, So	ects of Variables (System Size, Dynamics Equilibrium eps, Annealing Temperature, Simulation Temperature, Strain lid Thickness) on the Mechanical Properties of Amorphous	
		Silicon I	Dioxide (Tersoff Potential)	39
		2.3.1 S	ystem Size Effects	39
		2.3.2 D	Oynamics Equilibrium Time-steps Effects	40
		2.3.3 A	Annealing Temperature Effects	43
		2.3.4 S	imulation Temperature Effects	46
		2.3.5 S	train Rate Effects	49
		2.3.6 S	olid Thickness Effects	51
	2.4	The Effe	ects of Variables (System Size, Annealing Temperature, Strain	
		(ReaxFF	Potential)	53
		2.4.1 S	ystem Size Effects	53
		2.4.2 A	Annealing Temperature Effects	55
		2.4.3 S	train Rate Effects	59
	2.5	The Mee	chanical Properties of Amorphous Silicon Dioxide in Tersoff	
		Potentia	1	61

#### v

	2.6	The N Poton	Aechanical Properties of Amorphous Silicon Dioxide in Reaxff	62
	2.7	The N Struct	Aechanical Properties of the Amorphous Silicon Dioxide sure with Crack Existence (Tersoff)	65
		2.7.1	The Amorphous Silicon Dioxide Structure with Crack Existence	65
		2.7.2	The Vacuum Width Effecting the Mechanical Properties of the Material	67
		2.7.3	The Mechanical Properties of the Amorphous Silicon Dioxide Structure with Crack Existence	70
3	DE SIN	FORM	IATION AND FRACTURE MECHANICS OF A WALL CARBON NANOTUBE (SWCNT)	74
	$3.1 \\ 3.2$	The M Apply	Method to Create a Single-Wall Carbon Nanotube (SWCNT) . ring Uni-axial Tension Test to the Carbon Nanotube	75 76
		3.2.1	Calculate the Axial Stress Applied on a Nanotube During the Uni-axial Tension Test	78
		3.2.2	Calculate the Lateral Stress Applied on a Nanotube During the Uni-axial Tension Test	80
	3.3	The M (SWC	Mechanical Properties of a Single-Wall Carbon Nanotube (NT) in AIREBO Potential	82
		3.3.1	The Mechanical Properties of a Single-Wall Carbon Nanotube (SWCNT) in the Axial Direction	82
		3.3.2	The Mechanical Properties of a Single-Wall Carbon Nanotube (SWCNT) in the Lateral Direction	84
4	$\mathbf{CR}$	ACK ]	PROPAGATION IN CNT-SIO <sub>2</sub> NANOCOMPOSITES	86
	4.1	Interfa The F	acial Strength	86
	4.0	Silica	Structure with a Hole (Tersoff Potential)	88
	4.3	Silica	racture Mechanism of the $CNT-SiO_2$ Nanocomposite and the Structure with a Hole (Reaxff Potential) $\ldots \ldots \ldots \ldots$	92

	$4.4 \\ 4.5$	The Cohesive Strength Effects (Tersoff Potential)	93 96
	4.6	The Radius Effects (Tersoff Potential)	98
<b>5</b>	TH	E RADIUS EFFECTS ON SILICA STRUCTURE WITH A	110
	но	LE IN CONTINUUM SCALE	119
	$5.1 \\ 5.2$	The Mesh Convergence Study	119
		Continuum Scale	123
	5.3	The Radius Effects	127
6	CO	NCLUSIONS & FUTURE WORK	132
$\mathbf{R}$	EFE]	RENCES	136
$\mathbf{A}$	ppen	dix	
A	CO	HESIVE STRENGTH EFFECTS MECHANICAL	
	$\mathbf{PR}$	OPERTIES OF SILICA	141

### LIST OF TABLES

4.1	The area fraction of the nanotube in domain and its corresponding radius	99
5.1	The number of elements on domain and its corresponding mesh size.	121
5.2	The area fraction of the hole in domain and its corresponding radius.	127
A.1	The mechanical properties of the silica structure with a hole (first peak) and the mechanical properties of the CNT-SiO <sub>2</sub> nanocomposites by applying different cohesive strength (first peak).	141

### LIST OF FIGURES

1.1	Granites with different colors[2]	2
1.2	Boeing 777x and its composite wings[3]. $\ldots$ $\ldots$ $\ldots$	3
1.3	Specific Strength (Strength/Density) and Specific Modulus (Modulus/Density) of different materials.	4
1.4	Examples of nanomaterial. Left side is a carbon nanotube, fullerene is in the middle and left side is a layer of graphene	5
1.5	A diagrammatic sketch of a CNT reinforcement nanocomposite. Yellow circles are carbon nanotubes and blue square is matrix	6
1.6	A diagrammatic sketch of a CNT-SiO $_2$ nanocomposite. The yellow circle is carbon nanotube and the blue square is silica matrix. $~$ .	8
1.7	Modern glass skyscrapers	9
1.8	Bioactive Glass Surface Reaction[14]	10
1.9	(a)Windshield cracked. (b)Chicago tower block's 103rd floor glass viewing platform cracked under tourists' feet[15]. (c)iPhone's screen cracked. (d)Laptop's screen cracked.	11
1.10	Schematic of a silicon transistor, the purple layer is the insulator made from silicon dioxide.	12
1.11	A carbon-nanotube field-effect transistor $(FET)[18]$	13
1.12	Research approach (multi-scale).	14

1.13	An overview of the ReaxFF system energy components, from [25].	20
2.1	The structure of silicon dioxide, each Si atom is bonded with 4 Oxygen atoms. The Si-O bond length is 1.6 Å and the Si-O-Si angle is 144°.	25
2.2	Different views of the unit cell which contains $36 \text{ SiO}_2$ atoms. Here, red colored atoms are Si-atoms and blue colored atoms are O-atoms.	25
2.3	<b>a.</b> A single crystalline silicon dioxide system which contains 333, 396 atoms and the magnification of the structure. <b>b.</b> An amorphous silicon dioxide system which contains 333, 396 atoms and the magnification of the structure.	26
2.4	The changing of temperature, energy, stress and domain size during the annealing process. (a) Temperature $vs$ annealing time-steps (b) energy $vs$ annealing time-steps (c) stress $vs$ annealing time-steps (d) domain size $vs$ annealing time-steps	28
2.5	The changing of domain size, stress, energy and temperature during the static equilibrium. (a) Domain size $vs$ static equilibrium time-steps (b) stress $vs$ static equilibrium time-steps (c) energy $vs$ static equilibrium time-steps (d) temperature $vs$ static equilibrium time-steps	30
2.6	The changing of temperature, energy, stress and domain size during the annealing process. (a) Temperature $vs$ annealing time-steps (b) energy $vs$ annealing time-steps (c) stress $vs$ annealing time-steps (d) domain size $vs$ annealing time-steps	31
2.7	The changing of temperature, energy, stress and domain size during the <i>nve</i> relaxation process. (a) Temperature $vs$ <i>nve</i> relaxation time-steps (b) energy $vs$ <i>nve</i> relaxation time-steps (c) stress $vs$ <i>nve</i> relaxation time-steps (d) domain size $vs$ <i>nve</i> relaxation time-steps.	32

2.8	The changing of temperature, energy, stress and domain size during the process of setting target temperature. (a) Temperature $vs$ time-steps for setting target temperature (b) energy $vs$ time-steps for setting target temperature (c) stress $vs$ time-steps for setting target temperature (d) domain size $vs$ time-steps for setting target temperature	34
2.9	The changing of temperature, energy, stress and domain size during the <i>npt</i> stress removing process. (a) Temperature <i>vs npt</i> stress removing time-steps (b) energy <i>vs npt</i> stress removing time-steps (c) stress <i>vs npt</i> stress removing time-steps (d) domain size <i>vs npt</i> stress removing time-steps	35
2.10	<b>a.</b> Schematic showing a representative volume element and applied constant strain rate condition. <b>b.</b> Snapshots in sequence of different configurations of a brittle solid when a uni-axial tension test is applied. <b>c.</b> Typical stress-strain curve for brittle solid and the methods for calculating the maximum stress, Young's modulus and energy release.	36
2.11	<b>a1-d1.</b> Sequence of snapshots of an amorphous silicon dioxide structure which is applied to the uni-axial tension test. <b>a2-d2.</b> Sequence of snapshots of the stress( $\sigma_{xx}$ ) distribution in the amorphous silicon dioxide structure which is applied to the uni-axial tension test.	38
2.12	A super cell which contains 8 repeated unit cells $(m = 2)$	40
2.13	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of system size (m)	41
2.14	Simulation results on the maximum stress (fracture strength or $\sigma_{\text{max}}$ ), energy released (G) and Young's modulus (E) as a function of the dynamics equilibrium time-steps by using the system which contains 333, 396 atoms.	42

2.15	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the annealing temperature by using the system which contains 333, 396 atoms.	44
2.16	The atomic structures of silica after applying amorphous procedure with different annealing temperature (2,000K, 4,000K, 6,000K, 8,000K, 10,000K, 12,000K, 14,000K and 16,000K).	45
2.17	The stress <i>vs</i> strain curves for the amorphous silicon dioxide system with different annealing temperature (2,000K, 4,000K, 6,000K, 8,000K, 10,000K, 12,000K, 14,000K and 16,000K) applied during the amorphous procedure.	46
2.18	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the simulation temperature by using the system which contains 333, 396 atoms.	48
2.19	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the strain rate by using the system which contains 333, 396 atoms.	50
2.20	The ortho view of the structure which contains $1,008,000$ SiO <sub>2</sub> atoms.	51
2.21	Compare the mechanical properties between the structure 1 which contains 333, 396 atoms and the structure 2 which contains 1,008,000 atoms.	52
2.22	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of system size	54
2.23	The stress <i>vs</i> strain curves for the amorphous silicon dioxide systems which contain 86,000, 345,000, 540,000 and 1,000,000 atoms.	55

2.24	<b>a1-a4.</b> Sequence of snapshots of the system which contains 86,000 atoms is applied to the uni-axial tension test. <b>b1-b4.</b> Sequence of snapshots of the system which contains 540,000 atoms is applied to the uni-axial tension test.	56
2.25	The stress vs strain curves for the amorphous silicon dioxide system which contains 540,000 atoms with different annealing temperature(8,000K, 10,000K, 12,000K) applied	57
2.26	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the annealing temperature by using the system which contains 540,000 atoms.	58
2.27	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the strain rate by using the system which contains 540,000 atoms.	60
2.28	The stress $vs$ strain curves for the amorphous silicon dioxide system by applying different strain rate $(1.0 \times 10^{-6} femtosecond^{-1}, 5.0 \times 10^{-6} femtosecond^{-1}, 1.0 \times 10^{-5} femtosecond^{-1}, 5.0 \times 10^{-5} femtosecond^{-1}, 1.0 \times 10^{-4} femtosecond^{-1})$ .	61
2.29	The stress $vs$ strain curve and mechanical properties of amorphous silicon dioxide under uni-axial tension test at a strain rate of $10^{-3}ps^{-1}$ (vacuum, 300K) by using Tersoff potential. And sequence of snapshots of stress ( $\sigma_{xx}$ ) distribution in amorphous silicon dioxide structure.	62
2.30	The stress $vs$ strain curve and mechanical properties of amorphous silicon dioxide under uni-axial tension test at a strain rate of $10^{-6}$ fs <sup>-1</sup> (vacuum, 300K) by using Reaxff potential.	64
2.31	(a)The amorphous silicon dioxide structure with crack existence. (b)The magnification of the crack.	65

2.32	(a)The structure which dose not have vacuum space periodically repeat in the x direction. (b)The structure which has vacuum space periodically repeat in the x direction.	66
2.33	Picture $a - h$ corresponding to different vacuum width from $10\mathring{A}$ to $80\mathring{A}$	68
2.34	When the force is applied on the $xz$ -plane, the stress applied on the structure which has smaller area on the $xz$ -plane is larger than the stress applied on the simulation box which has larger area on the $xz$ -plane.	69
2.35	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the vacuum width	70
2.36	(a) The stress <i>vs</i> strain curves for the amorphous silicon dioxide with and without the crack existence. (b) The mechanical properties of the amorphous silicon dioxide with and without the crack existence.	71
2.37	$(a1 - a6)$ Sequence of snapshots of the stress $(\sigma_{yy})$ distribution in the material when the uni-axial tension test was applying. (b) Before the failure of the material, the stress was concentrating at the edge of the crack when the uni-axial tension test was applying.	73
3.1	The way graphene is wrapped is decided by the vector $C_h$ which is represented by a pair of indices $(n, m)$ . T is the tube axis, $a_1$ and $a_2$ are the unit vectors of the graphene sheet[50]	75
3.2	(a) The graphene nanoribbon wrapped in armchair direction to form an armchair nanotube. (b) The graphene nanoribbon wrapped in zigzag direction to form a zigzag nanotube	77
3.3	The top and front views of a nanotube, in which $P$ is the pressure tensor on $z$ direction, $L_x$ and $L_y$ are box length on $x$ and $y$ directions.	79

3.4	The top and right views of a nanotube, in which $P$ is the pressure tensor in $y$ direction, $L_x$ , $L_y$ and $L_z$ are box length on $x$ , $y$ and $z$ directions, $\sigma_{yy}$ is the nanotube lateral stress	81
3.5	(a) The stress $vs$ strain curve for an armchair carbon nanotube with $(n,m) = (20,20)$ $(d = 2.7 \text{ nm})$ under uni-axial tension test at a strain rate of $10^{-3} \text{ ps}^{-1}$ (vacuum, 1K) (b) The mechanical properties of the carbon nanotube	82
3.6	A sequence of snapshots of stress $(\sigma_{zz})$ distribution in an armchair carbon nanotube with $(n,m) = (20, 20)$ $(d = 2.7 \text{ nm})$ during the uni-axial tension test on the axial direction.	83
3.7	(a) The stress $vs$ strain curve for an armchair carbon nanotube with $(n,m) = (20,20) \ (d = 2.7 \text{nm})$ under uni-axial tension test in the lateral direction at a strain rate of $10^{-3} \text{ ps}^{-1}$ (vacuum, 1K) (b) The mechanical properties of the carbon nanotube in lateral direction.	84
3.8	A sequence of snapshots of stress $(\sigma_{yy})$ distribution in an armchair carbon nanotube with $(n, m) = (20, 20)$ $(d = 2.7 \text{nm})$ during the uni-axial tension test on the lateral direction.	85
4.1	Site-dependent electronic interaction between SiO <sub>2</sub> and CNT. The weakest interaction is identified at $x_0 = 18.25$ Å, and the strongest interaction is identified at $x_0 = 8.25$ Å. For all the cases, the LJ-parameters representing the two-body interaction are kept fixed to $\sigma = 3.0$ and $\epsilon = 0.050$ eV. The nanotube diameter is 7.52Å and its length is 16.32Å.	87
4.2	(a) The top view of the CNT-SiO <sub>2</sub> nanocomposite with $L_x = 1028\text{\AA}, L_y = 849\text{\AA}, L_z = 16.3201\text{\AA}, d = 178\text{\AA}, l_c = 100\text{\AA}$ and $l_n = 100\text{\AA}$ . (b) The front view of the CNT-SiO <sub>2</sub> nanocomposite. (c) The ortho view of the nanotube inserting into the silica matrix.	89
4.3	(a) The ortho view of the $CNT$ -SiO <sub>2</sub> nanocomposite and enlarged picture of the nanotube assembled in the silica matrix. (b) The ortho view of the silica structure with a hole and enlarged picture of the hole in the silica matrix.	90

4.4	1. The stress $vs$ strain curve of the CNT-SiO <sub>2</sub> nanocomposite with cohesive strength of 0.05ev under uni-axial tension test at a strain rate of $2.0 \times 10^{-4}$ ps <sup>-1</sup> (vacuum, 1K) by using Tersoff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO <sub>2</sub> nanocomposite (a1-f1). 2. The stress $vs$ strain curve of the silica structure with a hole under uni-axial tension test at a strain rate of $10^{-3}$ ps <sup>-1</sup> (vacuum, 1K) by using Tersoff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in the silica structure (a2-f2).	102
4.5	A typical stress $vs$ strain curve for the CNT-SiO <sub>2</sub> nanocomposite or the silica structure with a hole.	103
4.6	1. The stress $vs$ strain curve of the CNT-SiO <sub>2</sub> nanocomposite with cohesive strength of 0.05ev under uni-axial tension test at a strain rate of $10^{-3}$ ps <sup>-1</sup> (vacuum, 300K) by using Reaxff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO <sub>2</sub> nanocomposite (a1-f1). 2. The stress $vs$ strain curve of the silica structure with a hole under uni-axial tension test at a strain rate of $10^{-3}$ ps <sup>-1</sup> (vacuum, 300K) by using Reaxff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in the silica structure (a2-f2).	104
4.7	(a1) The first peak simulation results on the maximum stress $(\sigma_{\text{max1}})$ , energy released $(G_{c1})$ and Young's modulus $(E)$ as a function of the cohesive strength by deforming the CNT-SiO <sub>2</sub> nanocomposite. (b1) The second peak simulation results on the maximum stress $(\sigma_{\text{max2}})$ and energy released $(G_{c2})$ as a function of the cohesive strength by deforming the CNT-SiO <sub>2</sub> nanocomposite.	105
4.8	(a2) The first peak simulation results on the maximum stress $(\sigma_{\max 1})$ , energy released $(G_{c1})$ and Young's modulus $(E)$ by deforming the silica structure with a hole. (b2) The second peak simulation results on the maximum stress $(\sigma_{\max 2})$ and energy released $(G_{c2})$ by deforming the silica structure with a hole	106

4.9	(a3) The relative difference between the mechanical properties of the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference) for the first peak results. (b3) The relative difference between the mechanical properties of the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference) for the second peak results	107
4.10	(a1-a4) During the uni-axial tension test, a sequence of snapshots of stress $(\sigma_{yy})$ distribution in CNT-SiO <sub>2</sub> nanocomposite by applying 0.05ev cohesive strength. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress $(\sigma_{yy})$ distribution in CNT-SiO <sub>2</sub> nanocomposite by applying 0.1ev cohesive strength	108
4.11	(a1)-(a2) The first peak simulation results on the maximum stress $(\sigma_{\max 1})$ and energy released $(G_{c1})$ as a function of the cohesive strength by deforming the CNT-SiO <sub>2</sub> nanocomposite. (b1)-(b2) The second peak simulation results on the maximum stress $(\sigma_{\max 2})$ and energy released $(G_{c2})$ as a function of the cohesive strength by deforming the CNT-SiO <sub>2</sub> nanocomposite	109
4.12	(a) The first peak simulation results on the maximum stress $(\sigma_{\max 1})$ and energy released $(G_{c1})$ by deforming the silica structure with a hole. (b) The second peak simulation results on the maximum stress $(\sigma_{\max 2})$ and energy released $(G_{c2})$ by deforming the silica structure with a hole	110
4.13	(a1) The relative difference of $\sigma_{\text{max1}}$ between the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference). (a2) The relative difference of $G_{c1}$ between the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference). (b1) The relative difference of $\sigma_{\text{max2}}$ between the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference). (b2) The relative difference of $G_{c2}$ between the CNT-SiO <sub>2</sub>	111
	nanocomposite and the sinca structure with a noie (reference)	111

4.14	(a1-a4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO <sub>2</sub> nanocomposite by applying 0.005ev cohesive strength. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO <sub>2</sub> nanocomposite by applying 0.05ev cohesive strength	112
4.15	(a1-a4) During the uni-axial tension test, a sequence of snapshots of stress $(\sigma_{yy})$ distribution in CNT-SiO <sub>2</sub> nanocomposite by applying 0.1ev cohesive strength. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress $(\sigma_{yy})$ distribution in CNT-SiO <sub>2</sub> nanocomposite by applying 0.15ev cohesive strength	113
4.16	The CNT-SiO <sub>2</sub> nanocomposite with different nanotube radius (area fraction) set up (a1: $0.5\%$ , a2: $1.5\%$ , a3: $2.5\%$ , a4: $3.5\%$ , a5: $7\%$ , a6: $8\%$ , a7: $9\%$ , a8: $10\%$ ).	114
4.17	(a1) The first peak simulation results on the maximum stress $(\sigma_{\max 1})$ , energy released $(G_{c1})$ and Young's modulus $(E)$ as a function of the area fraction of the nanotube in domain by deforming the CNT-SiO <sub>2</sub> nanocomposite. (b1) The second peak simulation results on the maximum stress $(\sigma_{\max 2})$ and energy released $(G_{c2})$ as a function of the area fraction of the nanotube in domain by deforming the CNT-SiO <sub>2</sub> nanocomposite	115
4.18	(a2) The first peak simulation results on the maximum stress $(\sigma_{\max 1})$ , energy released $(G_{c1})$ and Young's modulus $(E)$ as a function of the area fraction of the hole in domain by deforming the silica structure with a hole. (b2) The second peak simulation results on the maximum stress $(\sigma_{\max 2})$ and energy released $(G_{c2})$ as a function of the area fraction of the hole in domain by deforming the silica structure with a hole. $\ldots$	116
4.19	(a3) The relative difference between the mechanical properties of the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference) for the first peak results. (b3) The relative difference between the mechanical properties of the CNT-SiO <sub>2</sub> nanocomposite and the silica structure with a hole (reference) for the second peak results.	117

4.20	(a1-a4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO <sub>2</sub> nanocomposite and the area fraction of the nanotube in domain is 3.0%. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO <sub>2</sub> nanocomposite and the area fraction of the nanotube in domain is 3.5%.	118
5.1	The top view of the silica structure with $L_x = 1028$ Å, $L_y = 849$ Å, $d = 103.2$ Å, $l_c = 100$ Å and $l_n = 100$ Å.	120
5.2	The silica structure with different mesh size. The total number of element on domain is (a)256 (b)540 (c)2143 (d)3606 (e)7928 (f)12777	121
5.3	Simulation results on the maximum stress (fracture strength or $\sigma_{\text{max}}$ ), energy released (G) and Young's modulus (E) as a function of number of elements on domain.	122
5.4	The cohesive zone ahead of a crack	124
5.5	(a1)(b1) The maximum principal stress in $y$ direction $(\sigma_n)$ distributes in the silica structure right before the crack propagation and the magnifying image of the crack. (a2)(b2) The maximum principal stress in $y$ direction $(\sigma_n)$ distributes in the silica structure right after the crack propagation and the magnifying image of the crack	125
5.6	The stress $vs$ strain curve of the silica structure with a hole $(R = 102.8 \text{ Å})$ under uni-axial tension test in the continuum scale. And sequence of snapshots of maximum principal stress $(\sigma_n)$ distribution in the silica structure (a-f).	126
5.7	The silica structure with different hole radius (area fraction) set up (a1: 1%, a2: 2%, a3: 3%, a4: 4%, a5: 5%, a6: 6%, a7: 7%). $\ldots$	130
5.8	Simulation results on the maximum stress (fracture strength or $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the hole radius.	131

6.1	The $CNT$ -SiO <sub>2</sub> nanocomposites with line nanotube configurations.	134
6.2	(a) The CNT-SiO <sub>2</sub> nanocomposite with triangle nanotube configuration. (b) The CNT-SiO <sub>2</sub> nanocomposite with square nanotube configuration. (c) The CNT-SiO <sub>2</sub> nanocomposite with pentagon nanotube configuration. (d) The CNT-SiO <sub>2</sub> nanocomposite with hexagon nanotube configuration	135

#### ABSTRACT

Carbon nanotube (CNT) based nanocomposites have gained great technological importance in recent years due to their outstanding structural, electronic, optical and thermal properties. However, the effect of nanotube on macroscopic properties of composites remains less understood. The underlying challenge is to characterize the complex interaction between nanotubes and the surrounding matrix which can depend on the interfacial strength of the nanotube and its diameter, as well as various scale-dependent mechanisms.

To address the challenge, this thesis develops a multiscale approach. The approach integrates simulations with density functional theory (DFT), molecular dynamics (MD), and the finite element (FE) method. DFT is used to compute fundamental material properties, MD to study sub-micron scale deformation mechanisms, and FEM to study longer length scale behavior. We also compare the FEM results with the MD results. The entire investigation has two parts: (a) investigation of interfacial strength, and (b) investigation of nanotube diameters, with a focus on their effects on macroscopic properties. For carrying out the investigations, we take silica (SiO<sub>2</sub>) as an example matrix material (due to its many critical applications) and explore the effect of nanotube reinforcement on stiffness, strength and toughness of CNT-SiO<sub>2</sub> nanocomposites.

For the interfacial strength study, the results show that nanotube delaminates when the interfacial strength is low enough and it fractures when the interfacial strength is high. The delamination process can therefore play a significant role in controlling the effective fracture strength and toughness of the CNT-SiO<sub>2</sub> nanocomposites. The condition for delimination is governed by an intricate site-dependent interaction between the nanotube and the SiO<sub>2</sub> matrix. Nonetheless, increasing interfacial strength improves the effective properties substantially. For example, a two-fold increase in interfacial strength increases effective strength by more than 7% and effective toughness by more than 16%. The overall influence is however nonlinear, and there is a corresponding mathematical relationship between the interfacial strength and effective strength or toughness. Additionally, we find that increasing nanotube diameter decreases stiffness and strength, but its effect on toughness is difficult to quantify.

Incorporating the atomistic information in a finite element based continuum framework, it is found that the macroscopic stress-strain response of a hole-SiO<sub>2</sub> nanostructure is inconsistent with the corresponding stress-strain response in MD simulation, although the bulk material properties in the finite element calculation are taken from the MD simulation. Therefore, this thesis concludes that developing multiscale computational approach is necessary to determine the stress-strain behavior of composites accurately as well as to predict the implication of nanostructure-reinforcement on macroscopic or effective properties of the nanocomposite.

## Chapter 1 INTRODUCTION

#### 1.1 Composite Material

A composite material is a material made from two or more materials which have different physical or chemical properties, and the newly combined composite material has distinguishing physical or chemical properties compare to its constituent materials. Composite material has two major categories, one is naturally occurring composite material, another is synthetic composite material. Naturally occurring composite material is everywhere in our life. One of the example is granite. Granite is an igneous rock with light color grains. It is mainly composed by quartz and feldspar with small amounts of amphiboles, mica and other minerals. These different constituent minerals give granite different colors like red, pink, gray or white[1]. The picture below shows granites with different colors:

Synthetic composite material is another major category of composite material. It has been widely used in many areas such as aerospace industry and automobile industry. One of the example is the composite wings made for Boeing new aircraft 777X.



Figure 1.1: Granites with different colors[2].

From the Fig.1.2, it can be seen that the wings of Boeing 777X are large, the composite wingspan of the 777X measures 71.7m and 6.95m[4] which are higher than the current model 777-9. With the wider and longer composite wings, they add a 7% improvement of fuel consumption compare to the 777-9[5]. But why those wings are made from composite materials, not the conventional materials? The answer is composite materials are stronger and lighter than many conventional materials. This is because composite materials have high strength-to-weight and high



Figure 1.2: Boeing 777x and its composite wings[3].

stiffness-to-weight ratios which are referred to as specific strength and specific modulus (property/density).

The Fig.1.3 shows the specific strength and specific modulus of different materials. It can be seen that, in longitude direction, the composite materials such as Carbon-epoxy T300/N5208-L and Carbon-epoxy AS/H3501-L have much higher specific strength and specific modulus than the conventional materials such as steel and aluminum alloy. On the other hand, we can see that Carbon-epoxy T300/N5208 have much lower specific modulus and specific strength in transverse direction than longitudinal direction. This means the mechanical properties of composite materials are direction dependent, and this property will be studied in section 3.3.



Figure 1.3: Specific Strength (Strength/Density) and Specific Modulus (Modulus/Density) of different materials.

#### 1.1.1 Nanocomposite

In section 1.1, we introduced the definition of composite materials which is a material made from two or more materials that have different physical or chemical properties. This definition also includes nanocomposite. However, in nanocomposite, at least one of the constituent material has to be a nanomaterial. What is nanomaterial? The definition of nanomaterial is not very clear. But in principle, a material which has at least one dimension is between 1-100 nm (the usual definition of nanomaterial. Fig.1.4 shows 3 typical examples of nanomaterial.



Figure 1.4: Examples of nanomaterial. Left side is a carbon nanotube, fullerene is in the middle and left side is a layer of graphene.

The carbon nanotube is carbon made, tube-shaped material and has the radius in nanometer scale. Fullerene is a carbon molecule in the shape of sphere, ellipsoid and others. Graphene is a carbon made 2 dimension material which has hexagonal lattice. Its thickness is from 0.35 to 1 nm[7]. Although they are very "small" and looks like a "fragile paper". However, those nanomaterials have remarkable physical properties. For example, carbon nanotubes have very high tensile strength 75 - 135 GPa (depending on tube chirality)[8] and Young's modulus 1.3 -0.4/+0.6 TPa (depending on tube chirality)[9]which are at least 100 times stronger and stiffer than steel, but only one-sixth as heavy[10]. Carbon nanotubes also have high electrical conductivity and thermal conductivity. Therefore, it has great potentials in semiconductor industry. And because the remarkable physical properties of nanomaterials, they give nanocomposites some special advantages compare to conventional composites. One of the advantage is that the area of the interface between the matrix and reinforcement phase of nanocomposite is much higher than conventional composite. Therefore, a small amount of nano-reinforcements can have a sufficient effect on macroscopic properties of a nanocomposite. For example, carbon nanotubes have been used as reinforcing agents to fabricate the biodegradable and biocompatible polymer polypropylene fumarate (PPF) for bone tissue engineering applications. The concentration of reinforcement agents is very low (0.2 weight %) but cause significant enhancement in the compressive and flexural mechanical properties of polymeric nanocomposites[11].

Another advantage of nanocomposites is lightweight. For example, the Fig.1.5 shows a diagrammatic sketch of a CNT reinforcement nanocomposite.



**CNT Reinforcement Nanocomposite** 

Figure 1.5: A diagrammatic sketch of a CNT reinforcement nanocomposite. Yellow circles are carbon nanotubes and blue square is matrix.

Form the Fig.1.5, it can be seen that the nanocomposite is assembled by inserting the nanotubes into the matrix, since there is no material inside these nanotubes. Therefore, inserting nanotubes can reduce the weight of nanocomposite because some of matrix material has been removed by inserting nanotubes, and along with carbon nanotube itself is a light weight material. Therefore, nanocomposites can be mechanically strong as well as light weight.

#### **1.1.2** CNT-SiO<sub>2</sub> Nanocomposite

In section 1.1.1, we introduced the definition of nanocomposites and their special properties. And in this section, I will introduce the main subject matter of this thesis:  $CNT-SiO_2$  nanocomposite. In Fig.1.5, we introduced the CNT reinforcement nanocomposite which is assembled by inserting the nanotubes into the matrix, and for  $CNT-SiO_2$  nanocomposite, the matrix material is silica. For better understanding the physical properties of  $CNT-SiO_2$  nanocomposite, in this thesis, we will study the  $CNT-SiO_2$  nanocomposite with only one carbon nanotube as shown in the Fig.1.6.

In section 1.1.1, we already introduced some remarkable and special physical properties of carbon nanotube. For CNT-SiO<sub>2</sub> nanocomposite, except carbon nanotube, another material is silica. What is silica? Why should we study silica? Is silica a special material which is worth to study? However, silica is not "special" at all, silica as well as SiO<sub>2</sub> is one of the most common chemical compound on earth, it is the main ingredient of sand. Actually, the mass of Earth's crust is 59 percent silica and more than 95 percent of the known rocks, the main constituent is silica[12]. The fused silica is called glass which can be formed by melting the crystal SiO<sub>2</sub> and then





Figure 1.6: A diagrammatic sketch of a  $CNT-SiO_2$  nanocomposite. The yellow circle is carbon nanotube and the blue square is silica matrix.

slow annealing to room temperature (see section 2.1.2 and section 2.1.3). Because its cheap raw material (sand) and some special physical properties, glass has been widely used in our life. Since glass is transparent and has high fracture strength. Therefore, in construction industry, lots of modern buildings have glass facades as shown in the Fig.1.7. And also, most of screens on electronic products are made of glass.

Glass also has been used in medical industry such as bioglass. Bioglass is a glass specifically composed of 45 mol % SiO<sub>2</sub>, 24.5 mol % CaO, 24.5 mol % Na<sub>2</sub>O, and 6.0 mol %  $P_2O_5[13]$ . Since bioglass has biocompatibility, it can be implanted into human bodies to repair bone injures and defects as shown in the Fig.1.8.

Although glass has many special physical properties, but since glass is brittle



Figure 1.7: Modern glass skyscrapers.

material, it fractures very easily. That is why when we package and ship glass items, we always have a warning label sticks outside the package said "Glass! Please handle with care!" Fracture of glass happens everyday, and it truly influences our life (see Fig.1.9).

How can we make glass more fracture resistance? The answer is we have to increase its ability to absorb energy and plastically deform before fracturing[16] which is increase its toughness. In order to increase the toughness of silica, the nantoube is inserted into the silica matrix as shown in the Fig.1.6. In this thesis, we will study how the nanotube geometry and the interface environment between the matrix and reinforcement phase effect the mechanical properties of CNT-SiO<sub>2</sub> nanocomposite. By exploiting those basic heterogeneity and engineering architectures of CNT-SiO<sub>2</sub>



Figure 1.8: Bioactive Glass Surface Reaction [14].

nanocomposite, we can explore novel pathways for generating new ideas of material design to maximize the toughness of  $CNT-SiO_2$  nanocomposite.

Fused silica also plays an important role in the semiconductor industry. Since fused silica has extremely good dielectric and insulating properties[17]. Therefore, it is a good example of insulators in transistor production as shown in the Fig.1.10.

For decades, we shrink the physical size of silicon transistors to improve the efficiency and speed of our computer chips. However, we have already reached a point where the massive efforts we put to decrease the dimensions of silicon transistor but very limit gains in performance due to the issue of quantum leap. Researchers are pursing many ways to prevent the quantum leap of electrons between transistors.



Figure 1.9: (a)Windshield cracked. (b)Chicago tower block's 103rd floor glass viewing platform cracked under tourists' feet[15]. (c)iPhone's screen cracked. (d)Laptop's screen cracked.

And one way to solve this issue is to modify the materials and structures of current silicon transistors to improve the electronic properties of the device[18]. Therefore, the idea of carbon-nanotube field-effect transistor (FET) is generated as shown in the Fig.1.11.

From the Fig.1.11, we can see that the current-carrying channel is replaced



Figure 1.10: Schematic of a silicon transistor, the purple layer is the insulator made from silicon dioxide.

from silicon to carbon nanotubes [18] and carbon nanotubes lies on the glass insulator. Therefore, it is very important to understand the interface environment between the carbon nanotubes and the glass insulator, and how it effects the performance of the transistor. Right now, flexible electronic products are very popular such as flexible smart phone. However, we still don't know if the transistor is under bending, how the interface environment between the carbon nanotubes and the glass insulator effects the performance of transistor. This is another reason we want to study the CNT-SiO<sub>2</sub> nanocomposite under extreme conditions. By understanding the nanotubes and the interface environment between the matrix and reinforcement phase effect the mechanical properties of CNT-SiO<sub>2</sub> nanocomposite, we can explore novel pathways for generating new ideas of material design to improve the performance of carbon-nanotube field-effect transistor.



Figure 1.11: A carbon-nanotube field-effect transistor (FET)[18].

#### 1.1.3 Research Objectives and Approach

In section 1.1.2, we introduced  $\text{CNT-SiO}_2$  nanocomposite and why we should study it. However, in real life, it is a challenging and expensive task to preciously control the dimension of nanotubes and the interfacial interactions between the matrix and reinforcement phase. Therefore, a versatile computational approach through multiscale molding is offered. To enable the investigation at multiple length scales, the approach integrates simulations with density functional theory (DFT), molecular dynamics (MD), and the finite element (FE) method as shown in the Fig.1.12.

- 1. DFT
  - (a) Investigate the interfacial strength between CNT and silica
  - (b) Investigate the equilibrium distance between CNT and silica
- 2. MD

# **Research approach** (multi-scale)



Figure 1.12: Research approach (multi-scale).

- (a) Investigate the sub-micron deformation of CNT-silica system
- (b) Investigate the effect of interfacial strength and nanotube diameter on macroscopic strength, toughness and stiffness of CNT-SiO<sub>2</sub> nanocomposite
- (c) Investigate the atomistic mechanisms of  $CNT-SiO_2$  nanocomposite
- 3. FEM
  - (a) Investigate the sub-micron deformation of CNT-silica system
  - (b) Investigate the effect of nanotube diameter on macroscopic strength, toughness and stiffness of CNT-SiO<sub>2</sub> nanocomposite
(c) Checking continuum approximations by comparing with MD results

# 1.2 LAMMPS

In this study, LAMMPS was used to carry out the molecular dynamics simulations. LAMMPS (*Large – scale Atomic/Molecular Massively Parallel Simulator*) is a program developed by Sandia National Laboratories[27]. By using the commands provided by LAMMPS, different physical and mechanical phenomena was simulated. In this section, some key LAMMPS commands will be introduced to develop a better understanding of the MD simulations.

# 1.2.1 fix box/relax command

When  $fix \ box/relax$  command was carried out to the system, the external stress tensor is applied to the simulation box to reach the minimization of the potential energy. And the changing of the box size and shape during the minimization can let the final configuration be both the potential energy minimization and the equally between system pressure tensor and the specified external tensor[27]. In this study, the *fix box/relax* command was used, for example in section 2.1.2, 2.1.3.

# 1.2.2 fix npt command

When fix npt command was carried out to the system, the number of atoms, the pressure of the system and the temperature of the system should keep as constants. By using this command, we can control the pressure and the temperature of the system and let the system reach the isothermal-isobaric state [27]. In this study, the fix npt command was used, for example in section 2.1.2 and section 2.2.

# 1.2.3 fix nvt command

When  $fix \ nvt$  command was carried out to the system, the number of atoms, the volume of the system and the temperature of the system should keep as constants. By using this command, we can control the volume and the temperature of the system and let the system reach the canonical state[27]. In this study, the *fix nvt* command was used, for example in section 2.1.2.

# 1.2.4 fix nve command

By performing constant nuclear integration, the position and velocity of atoms in the system are updated in each timestep to create a system trajectory consistent with the microcanonical ensemble[27]. In this study, the *fix nuclear* command was used, for example in section 2.1.3.

# 1.2.5 fix deform command

By using the *fix deform* command, we can change the volume and/or shape of the simulation box during the molecular dynamics simulation[27]. In this study, the *fix deform* command was used to carry out the uni-axial tension test based on the equation 2.1 and which will be detailedly introduced in section 2.2.

## **1.3** Interatomic Potential

In a given system, interatomic potentials are mathematical functions for calculating the potential energy of atoms with certain positions[19]. The general form of interatomic potential for a system of N particles is:

$$E = \sum_{i} V_1(r_i) + \sum_{i < j} V_2(r_i, r_j) + \sum_{i < j < k} V_3(r_i, r_j, r_k) + \dots$$
(1.1)

The first term is single-particle potential that describes external forces to the entire atomic system, the second term is a 2-body potential (or pair potential) capturing interactions involving all possible set of two particles, and the third term is a 3body potential term that captures interactions involving all possible set of three particles[20].

## 1.3.1 Tersoff Interatomic Potential

For MD simulations, one of the interatomic potential we used is Tersoff potential [21], which has been used for studying a range of atomic systems [22]. The potential is based on the idea that the strength of a chemical bond depends on the bonding environment[23], for example, an atom has more neighbors will form weaker bond than an atom has less neighbors. The general form of the Tersoff potential is:

$$E = \sum_{i} E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \tag{1.2}$$

And the general form to represent the boundary energy  $(V_{ij})$  is:

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})]$$
(1.3)

From equation 1.2, it can be seen that the potential energy is the combination of site energy  $E_i$  or bonding energy  $V_{ij}$ . And in equation 1.3,  $r_{ij}$  is the distance between atoms *i* and atom *j*,  $f_A$  is the attractive pair potential,  $f_R$  is the repulsive pair potential, and  $f_C$  is a smooth cutoff function.  $f_A$  and  $f_R$  can be represented by following equations:

$$f_R(r) = Ae^{(-\lambda_1 r)} \tag{1.4}$$

$$f_A(r) = -Be^{(-\lambda_2 r)} \tag{1.5}$$

And the smooth cutoff function  $f_C$  can be represented by following equations:

$$f_C(r) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin[\frac{\pi}{2}(r - R)/D] & R - D < r < R + D \\ 0 & r > R + D \end{cases}$$
(1.6)

As we introduced above, the Tersoff potential is based on the idea that the strength of a chemical bond depends on the bonding environment[23] and this dependence is expressed by  $b_{ij}$ :

$$b_{ij} = \frac{1}{(1+\beta^n \zeta_{ij}^n)^{1/2n}}$$
(1.7)

The term  $\zeta_{ij}$  defines the number of atom *i* in the effective coordination:

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ij}) g(\theta_{ijk}) e^{[\lambda_3^3(r_{ij} - r_{ik})^3]}$$
(1.8)

And finally the suitable function  $g(\theta)$  is represented by following equation:

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (h - \cos \theta)^2]}$$
(1.9)

A(eV) from equation 1.4, B (eV) from equation 1.5,  $\lambda(\mathring{A}^{-1})$  from equation 1.4,1.5,1.8,  $\beta$  from equation 1.7, n from equation 1.7, c from equation 1.9, d from equation 1.9, hfrom equation 1.9, R ( $\mathring{A}$ ) from equation 1.6 are parameters for the Tersoff potential, and the value of the parameter is depended on the atom type.

# 1.3.2 The Reactive Force-field (ReaxFF) Interatomic Potential

For comparison with Tersoff results, we have also carried out some calculations by using the ReaxFF interatomic potential [24]. The ReaxFF potential is a general bond-order-dependent potential. By using the Coulomb and Morse (van der Waals) potentials on one hand and quantum chemical calculations on the other hand, this potential can accurately model reactive events (continuous bond formation and breaking) in larger scale system by using lower computational cost compare to quantum mechanics (QM) level calculations [24][25]. The ReaxFF overall system energy is described by the following:

$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{Specific} \quad (1.10)$$

 $E_{bond}$  is the energy relates to forming bonds between atoms.  $E_{angle}$  and  $E_{tors}$  are the three-body bending interaction and four-body torsion interaction.  $E_{over}$  is an energy penalty to prevent the number of bond an atom forming is larger than the number of electrons it needs to fill its outer shell (an over coordinated atom).  $E_{Coulomb}$  is electrostatic interactions characterizing by the Coulomb law, and  $E_{vdWaals}$  is Van der Waals interactions characterizing by the Lennard-Jones interactions. Both of them are non-bonded interactions.  $E_{Specific}$  are some specific terms represented in system[25].

From Fig.1.13, we can see that the potential is divided into two parts, first part is



Figure 1.13: An overview of the ReaxFF system energy components, from [25].

bonded interactions and the second part is no-bonded interactions. For the bonded interactions, one of the assumption in ReaxFF potential is that the bond order between two atoms can be calculated directly from interatomic distance by using the equation below:

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}$$
  
= exp[ $p_{bo1}(\frac{r_{ij}}{r_0^{\sigma}})^{p_{bo2}}$ ] + exp[ $p_{bo3}(\frac{r_{ij}}{r_0^{\pi}})^{p_{bo4}}$ ] + exp[ $p_{bo5}(\frac{r_{ij}}{r_0^{\pi\pi}})^{p_{bo6}}$ ] (1.11)

From equation 1.11, we can see that  $\sigma$  bonds,  $\pi$  bonds and  $\pi\pi$  bonds are distinguished by ReaxFF in calculating the bond orders.  $BO_{ij}$  is the bond order between a pair of atoms *i* and *j*,  $r_{ij}$  is interatomic distance,  $r_o$  terms are equilibrium bond lengths and  $p_{bo}$  terms are empirical parameters. The bonded interaction and non-bonded interaction are calculated independently and both are calculated without exception [25].

# 1.3.3 The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) Potential

In this study, AIREBO potential was used to carry out calculations for a system of carbon atoms[26]. This potential is based on the idea that the total potential energy of system is represented by the sum of nearest-neighbour pair interactions which depend not only on the distance between atoms but also on their local atomic environment[21]. The general form of the AIREBO potential is:

$$E = \frac{1}{2} \sum_{i} \sum_{j \neq i} (E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{kijl}^{tors})$$
(1.12)

From equation 1.12, we can see that AIREBO potential can be represented by a sum of covalent bonding REBO interactions  $(E_{ij}^{REBO})$ , LJ terms  $(E_{ij}^{LJ})$  and torsion interactions  $(E_{kijl}^{tors})$ . The term covalent bonding REBO interactions  $(E_{ij}^{REBO})$  is described through following equation[26]:

$$E_{ij}^{REBO} = V_{ij}^{R}(r_{ij}) + b_{ij}V_{ij}^{A}(r_{ij})$$
(1.13)

In equation 1.13,  $V_{ij}^R$  and  $V_{ij}^A$  are repulsive and attractive pairwise potentials determined by the atom types (carbon or hydrogen) of atoms *i* and *j*, and that depend only on  $r_{ij}$  the distance between the two atoms *i* and *j*.  $V_{ij}^{LJ}$  is the traditional LJ term[26]:

$$V_{ij}^{LJ} = 4\epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)$$
(1.14)

The torsion interactions  $(E_{kijl}^{tors})$  is an explicit 4-body potential that describes various dihedral angle preferences in hydrocarbon system[26]:

$$E_{kijl}^{tors} = w_{ki}(r_{ki})w_{ij}(r_{ij})w_{jl}(r_{jl})V^{tors}(\omega_{kijl})$$

$$(1.15)$$

The AIREBO potential will be used to simulate Carbon Nanotube (CNT) systems (see section 3.3)

# Chapter 2

# DEFORMATION AND FRACTURE MECHANICS OF AMORPHOUS SILICON DIOXIDE (GLASS)

Glass is a non-crystalline amorphous solid has been widely used in housing and buildings, appliances and electronics, medical technology and biotechnology etc. Since glass is an amorphous material, therefore in molecular dynamics, it has difficult to present the accurate mechanical properties and fracture behaviors compare to the real life observation. Ningbo et al. studied the fracture properties of amorphous silicon dioxide by using Tersoff potential [28]. Yuan et al. studied the mechanical properties of the amorphous silica from bulk to nanowire by using pair-wise BKS potential<sup>[29]</sup>. Those potentials can well represent the Young's modulus of the silica. However, for the maximum strength, their presenting values are inaccurate due to the complicated fracture mechanism of the amorphous structure. Therefore, an alternative potential needs to be found and Reaxff potential is one of the choice. Buehler et al. studied the crack propagation in silicon by using both Tersoff potential and Reaxff potential [30]. The results show that the Reaxff potential can reproduce the brittle fracture and which is comparable with experimental observation due to its special relationship with quantum mechanical (QM) methods. The Reaxff potential has also developed for the  $SiO_2$  system. Chowdhury et al. studied the mechanical properties of silica glass by using  $\operatorname{Reax} FF[31]$ . And also Yu et al. revisited the current program for improving predictions of glass structure and properties through Reaxff potential[32]. Both of them conclude that due to the complexity of the amorphous structure and variety of the amorphous process. Still the mechanical properties of silica such as maximum strength or Young's modulus can not accurately present in their studies.

In this chapter, we will discuss different ways to amorphous a crystal silicon dioxide system to a silica system in molecular dynamics simulations by using Tersoff and Reaxff potentials. Then, the mechanical properties and the fracture mechanics of the silica system will be studied by using both Tersoff and Reaxff potentials.

# 2.1 A Method to Create an Amorphous Silicon Dioxide System2.1.1 A Method to Create a Single-crystalline Silicon Dioxide Unit Cell

The structure of silicon dioxide shows tetrahedral coordination. The Si atom is in the center of the structure and it is bonded with 4 Oxygen atoms. The Si-O bond length is 1.6 Å and the Si-O-Si angle is 144° [33]. The structure of the silicon dioxide is shown in Fig.2.1:

Then, based on the structure of silicon dioxide (Fig.2.1), a unit cell is created. The unit cell contains 36 silicon dioxide atoms and the volume of the unit cell is  $9.836 \times 8.5182258 \times 5.407$  Å. Fig.2.2 shows different views of the unit cell.

The *unit cell* will be used for constructing larger super-cells for the MD simulations and this will be introduced in section 2.3.1.



Figure 2.1: The structure of silicon dioxide, each Si atom is bonded with 4 Oxygen atoms. The Si-O bond length is 1.6 Å and the Si-O-Si angle is 144°.



Figure 2.2: Different views of the unit cell which contains 36 SiO<sub>2</sub> atoms. Here, red colored atoms are Si-atoms and blue colored atoms are O-atoms.

# 2.1.2 The Thermal Annealing Method to Create an Amorphous Silicon Dioxide System (Tersoff Potential)

Unlike a single-crystalline silicon dioxide system which unbroken crystal lattice is continually repeated to the edges of the structure [34], the amorphous silicon dioxide system is lacking a clear crystal structure in the long-range order [35]. The Fig.2.3 shows the structure difference between single-crystalline silicon dioxide and amorphous silicon dioxide system.



Figure 2.3: a. A single crystalline silicon dioxide system which contains 333, 396 atoms and the magnification of the structure. b. An amorphous silicon dioxide system which contains 333, 396 atoms and the magnification of the structure.

Before amorphous the system, it is necessary to carry out the relaxation procedure. The purpose of the relaxation is to let every atom in the system reach its equilibrium. The relaxation has 2 steps. The first step is the static equilibrium [36]. In this case, the velocity of all atoms are 0 and the external stress tensor is applied to the simulation box to reach both the potential energy minimization and the equally between system pressure tensor and the specified external tensor[27] (see section1.2.1). The second step is the dynamics equilibrium, in which random velocities are set for all atoms and isotherm-isobaric state is desired to reach (see section1.2.2) [36][27]. In this case, the temperature is set as a constant at 300 K and the external pressure in x, y and z directions are set at 0 bar, then specific time-steps are set to let the system have enough time to reach the isotherm-isobaric state.

To reach the amorphous state, the thermal annealing method is applied to the single-crystalline silicon dioxide system[37]. In this case, the single-crystalline silicon dioxide system is melted by sudden increase the temperature of the system from 300K to 12,000K, and then annealed by slowly cooling it back to 300 K(see section1.2.3). The temperature sudden increase can make atom position distort then make sure the randomization of the single-crystalline, and then the cooling process can relieve residual internal stress introduced during the melting process. In this section, we will study how the system energy, domain size, stress and temperature change during the annealing process by using a single crystalline silicon dioxide system contains 333,396 atoms. In the annealing process, the dynamics equilibrium time-steps is 90,000 and melting temperature is 12,000K. The system energy, domain size, stress and temperature are recorded during the annealing process. The results are shown in the Fig.2.4. From the Fig.2.4(a), it can be seen that the temperature suddenly

increases at the beginning, then slowly and linearly decreases to room temperature. This is due to the atoms in the system have to resale their velocities in a timespan of (roughly) 0.1 picosecond to relax the temperature. And with the decreasing of the temperate, the total energy also decreases slowly and linearly as shown in the Fig.2.4(b). From the Fig.2.4(c), it can be seen that the stress suddenly increases at the beginning which is due to the temperature increase. Then with the linearly and slowly decreasing of the temperature, the residual stress is slowly relieved. And finally, the system domain size is keep as a constant due to the performance of fix nvt command (see section 1.2.3).



Figure 2.4: The changing of temperature, energy, stress and domain size during the annealing process. (a) Temperature vs annealing time-steps (b) energy vs annealing time-steps (c) stress vs annealing time-steps (d) domain size vs annealing time-steps.

After thermal annealing, the external stress tensor is applied to the simulation box (static equilibrium) to reach both the potential energy minimization and the equally between system pressure tensor and the specified external tensor[27] (see section1.2.1). From the Fig.2.5(a), it can be seen that at the beginning, the size of the simulation box decreases. This is because the external stress tensor is applied to the system to let the simulation box shrink to offset the remained tensile stress in the system, as shown in the Fig.2.5(b). From the Fig.2.5(c), it can be seen that the energy is minimized during the static equilibrium. And finally, from the Fig.2.5(d), the temperature is a constant. After the static equilibrium, the amorphous system is created as shown in the Fig.2.3b and the system is ready to apply the uni-axial tension test which will introduce in section 2.2.

# 2.1.3 The Thermal Annealing Method to Create an Amorphous Silicon Dioxide System (ReaxFF Potential)

For the ReaxFF potential, the first step to create an amorphous silicon dioxide system is the static equilibrium [36]. By applying the static equilibrium process, the velocities of all atoms are equal to 0 and the external stress tensor is applied to the simulation box to reach both the potential energy minimization and the equally between system pressure tensor and the specified external tensor[27] (see section1.2.1).

The second step is the thermal annealing process. In this case, the singlecrystalline silicon dioxide system is annealed by sudden increasing the temperature to 12,000K and then cool it back slowly to 1K(see section 1.2.3).



Figure 2.5: The changing of domain size, stress, energy and temperature during the static equilibrium. (a) Domain size vs static equilibrium time-steps (b) stress vs static equilibrium time-steps (c) energy vs static equilibrium time-steps.

From the Fig.2.6(a), it can be seen that during the thermal annealing process, the temperature suddenly increases, and then slowly and linearly cool it back to 1K. This is due to the atoms in the system have to resale their velocities in a timespan of (roughly) 50 femtoseconds to relax the temperature. And with decreasing of



Figure 2.6: The changing of temperature, energy, stress and domain size during the annealing process. (a) Temperature vs annealing time-steps (b) energy vs annealing time-steps (c) stress vs annealing time-steps (d) domain size vs annealing time-steps.

the temperate, the total energy also slowly and linearly decreases as shown in the Fig.2.6(b). From the Fig.2.6(c), it can be seen that at the beginning, the stress suddenly increases due to the increasing of temperature, then with the slow decreasing temperature, the residual stress is slowly relieved. And finally, the domain sizes are keeping as constants due to the performance of fix nvt command (see section 1.2.3).



Figure 2.7: The changing of temperature, energy, stress and domain size during the nve relaxation process. (a) Temperature vs nve relaxation time-steps (b) energy vs nve relaxation time-steps (c) stress vs nve relaxation time-steps (d) domain size vs nve relaxation time-steps.

After the thermal annealing process, the solid is relaxed by carrying out the fix nve command (see section 1.2.4).

From the Fig.2.7, it can be seen that by applying the fix nve relaxation process, the energy linearly decreases in a neglected amount and the temperature

is convergence. This means the system performs a constant nve integration to update position and velocity for atoms in the group each timestep[27] to reach the temperature equilibrium (see section 1.2.4). And at the same time, the stress and the domain sizes are keeping as constants. After the relaxation process, the *fix nvt* command (see section 1.2.3) is used to increase the current temperature (which is the equilibrium temperature) to the target temperature (which is 300K).

From the Fig.2.8(a), we can see that the system temperature is at 300K, and from the Fig.2.8(c), the residual stress is still remained in the system due to the restriction of the domain sizes. Therefore, the *fix npt* stress removing process (see section 1.2.2) is executed to let the system reach the isotherm-isobaric state. In this case, the temperature is set as a constant at 300K as shown in the Fig.2.9(a) and the external pressure on x, y and z directions are set at 0bar to remove the residual stress as shown in the Fig.2.9(c), then specific time-steps are set to let the system have enough time to reach the dynamics equilibrium.

After the stress removing process, the system is ready to apply the uni-axial tension test, and this will be introduced in the section 2.2.

# 2.2 Applying Uni-axial Tension Test to the Amorphous Silicon Dioxide Structure

After amorphous the silicon dioxide system, the uni-axial tension test is applied to the system[38]. Before the uni-axial tension test, the temperature is set as a constant at 300K and the external pressure on y and z directions are set at



Figure 2.8: The changing of temperature, energy, stress and domain size during the process of setting target temperature. (a) Temperature vs time-steps for setting target temperature (b) energy vs time-steps for setting target temperature (c) stress vs time-steps for setting target temperature (d) domain size vs time-steps for setting target temperature.

Obar(see section 1.2.2). During the uni-axial tension test, the velocity of x-direction displacement is held as a constant (constant strain rate) as shown in Fig. 2.10 (a). The Fig 2.10 (b) shows how the brittle solid (for example: glass) respond when the uni-axial tension test was applied. We can see that when the length in the loading



Figure 2.9: The changing of temperature, energy, stress and domain size during the npt stress removing process. (a) Temperature vs npt stress removing time-steps (b) energy vs npt stress removing time-steps (c) stress vs npt stress removing time-steps (d) domain size vs npt stress removing time-steps.

direction (x direction) is continuous increasing, the length in another direction (y direction) is decreasing because of the Poisson's effect [39] until the solid is fracture. Then, the stress vs strain curve is recorded, the Fig.2.10 (c) is a stress vs strain curve for a brittle solid. From the stress vs strain curve, the mechanical properties of the solid can be calculated. The maximum stress is the maximum value of  $\sigma_{xx}$ , the Young's modulus is the slope of the stress vs strain curve and the energy release is the integral of the stress vs strain curve.



Figure 2.10: a. Schematic showing a representative volume element and applied constant strain rate condition. b. Snapshots in sequence of different configurations of a brittle solid when a uni-axial tension test is applied.
c. Typical stress-strain curve for brittle solid and the methods for calculating the maximum stress, Young's modulus and energy release.

To control the speed of the displacement, the constant strain rate is applied (see section 1.2.5)[40]. The length of the solid L in loading direction as a function of time will change as:

$$L(t) = L_0 \times (1 + \text{erate} \times \Delta t)[41]$$
(2.1)

 $L_0$  is the original length of the solid in load direction, erate is the stain rate and dt is the elapsed time. For example, if erate is 0.01 and time units are picoseconds, this means the length of the solid in loading direction will increase by 1% of its original length in every picosecond.

The Fig.2.11 shows a sequence of snapshots of an amorphous silicon dioxide structure applied to the uni-axial tension test. From the Fig.2.11 a2-d2, we can see that the distribution of the stress ( $\sigma_{xx}$ ) in the structure. The Fig.2.11 a2 shows the stress distribution of the silicon dioxide structure right before the failure, we can see that the stress distribution in the whole structure is very high. Then from the Fig.2.11 b2-d2, it can be seen that the failure of the structure and the releasing of the stress when the crack is appeared and grow in the solid.



Figure 2.11: a1-d1. Sequence of snapshots of an amorphous silicon dioxide structure which is applied to the uni-axial tension test. a2-d2. Sequence of snapshots of the stress( $\sigma_{xx}$ ) distribution in the amorphous silicon dioxide structure which is applied to the uni-axial tension test.

2.3 The Effects of Variables (System Size, Dynamics Equilibrium Timesteps, Annealing Temperature, Simulation Temperature, Strain Rate, Solid Thickness) on the Mechanical Properties of Amorphous Silicon Dioxide (Tersoff Potential)

## 2.3.1 System Size Effects

In this section, we will study the effects of system size on the mechanical properties of amorphous silicon dioxide. The total number of atoms in a super-cell containing m number of unit cells in each direction is:

$$N = (m \times m \times m) \times (\text{atoms in the unit cell})$$
(2.2)

$$= m^3 \times 36 \tag{2.3}$$

From the Fig.2.12, we can see that when m = 2, the unit cell contains 36 atoms will be periodically repeated 1 time on its x, y and z directions. Then the total number of atoms in the periodic system (super cell) will be  $m^3 \times 36 = 2^3 \times 36 = 288$ . In this section 20 super-cells were created (corresponding to  $m = 2 \rightarrow 21$ ).

After amorphous the 20 super-cells (see section 2.1.2), the uni-axial tension test was applied (see section 2.2). Then, maximum stress, energy release and Young's modulus were calculated for each case (see section 2.2). The results are shown in the Fig.2.13, it can be seen that when m increases, the maximum stress, energy release and Young's modulus are convergence. This means the system size should be large enough to eliminate the effects on mechanical properties of amorphous silicon dioxide.



Figure 2.12: A super cell which contains 8 repeated unit cells (m = 2)

# 2.3.2 Dynamics Equilibrium Time-steps Effects

Dynamics equilibrium is a state that all the atoms in the structure are isothermisobaric and which was introduced previously in section 2.1.2. In this section, we will study the effects of dynamics equilibrium time-steps on the mechanical properties of silica. We applied 10,000, 30,000, 50,000, 70,000 and 90,000 dynamics equilibrium time-steps before the amorphous procedure (see section 2.1.2) and then the uni-axial tension test (see section 2.2) was applied to the system. After that, maximum stress, energy release and Young's modulus were calculated for each time-steps set up.

The results are shown in the Fig 2.14, it can be seen that the dynamics



Figure 2.13: Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of system size (m).

equilibrium time-steps have neglected effects on the maximum stress, energy release and Young's modulus of silica. Therefore, 10,000 time-steps are sufficient to let the structure reach the dynamics equilibrium.



**Figure 2.14:** Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the dynamics equilibrium time-steps by using the system which contains 333, 396 atoms.

#### 2.3.3 Annealing Temperature Effects

To create an amorphous silicon dioxide structure, the thermal annealing method is applied to the system which was previously introduced in section 2.1.2. Through sudden increasing the temperature of the system then slowly cooling it back to room temperature, the amorphous structure is created. In this section, different annealing temperature was applied to the system (2,000K, 4,000K, 6,000K, 8,000K, 10,000K, 12,000K, 14,000K and 16,000K) to investigate the effects of annealing temperature on the mechanical properties of silica, and for each annealing temperature set up, the amorphous procedure (see section 2.1.2) and then the uni-axial tension test (see section 2.2) were applied to the system. After that, maximum stress, energy release and Young's modulus were calculated for each annealing temperature set up.

The results are shown in the Fig.2.17. From the stress strain curves for the 2,000K and 4,000K cases in the Fig.2.17, we can clearly see that the silica is hardening during the uni-axial tension test and which is not a typical property of a brittle material. And this finding can also be seen in the Fig.2.15, when the annealing temperature set up is 2,000K and 4,000K, the maximum stress, energy release and Young's modulus are much higher compare to other cases due to the material hardening. If we take a close look at the atomic structure of silica in each case (see Fig.2.16), we can see that after the amorphous procedure was applied with annealing temperature of 2,000K and 4,000K, the atomic structures of silica still contain some kind of crystal structures, and which means the silica systems are not fully amorphous. Therefore, we can conclude that the un-fully amorphous silica structure due to low annealing temperature applied can lead to unphysical material hardening



Figure 2.15: Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the annealing temperature by using the system which contains 333, 396 atoms.

when load is applied, and to avoid such situation, the annealing temperature has to be higher than 6,000K.



Figure 2.16: The atomic structures of silica after applying amorphous procedure with different annealing temperature (2,000K, 4,000K, 6,000K, 8,000K, 10,000K, 12,000K, 14,000K and 16,000K).



**Figure 2.17:** The stress *vs* strain curves for the amorphous silicon dioxide system with different annealing temperature (2,000K, 4,000K, 6,000K, 8,000K, 10,000K, 12,000K, 14,000K and 16,000K) applied during the amorphous procedure.

# 2.3.4 Simulation Temperature Effects

The simulation temperature is the temperature of the system when the uniaxial tension test is performing (see section 2.2). To investigate the effects of simulation temperature on the mechanical properties of the material, different simulation temperature was applied to the system (100K, 300K, 600K, 900K, 1200K). For each simulation temperature set up, the uni-axial tension test was applied to the system. Then, maximum stress, energy release and Young's modulus were calculated. The results are shown in the Fig.2.18, it can be seen that when the simulation temperature increases, the mechanical properties of the material undergo reduction at high temperatures. This is because the higher temperature creates stronger thermal vibration which makes the material less stiff [42]. From the Fig.2.18, it can be seen that there is a linear relationship between the maximum stress and simulation temperature. Then, the linear function of maximum stress ( $\sigma_{max}$ ) dependents on the simulation temperature (T) is written as:

$$\sigma_{\max}(T) = \alpha T + \sigma_{\max}(0) \tag{2.4}$$

Where  $\alpha$  is the slope of the equation and  $\sigma_{\max}(0)$  is the maximum stress at 0K, and based on the equation of slope, we can get  $\alpha$  equals to -0.0185. Then the equation 2.4 became:

$$\sigma_{\max}(T) = -0.0185T + \sigma_{\max}(0) \tag{2.5}$$

From the Fig.2.18, it can be seen that when the simulation temperature is 1200K, the maximum stress is 33.602 Gpa. Bring those 2 values into the equation 2.5, we can calculate the  $\sigma_{\max}(0)$ :

$$\sigma_{\max}(0) = 33.602 + 0.0185 \times 1200 \tag{2.6}$$

$$= 55.8Gpa \tag{2.7}$$

Finally, the linear function of maximum stress  $(\sigma_{\max})$  dependents on the simulation temperature (T) is written as:

$$\sigma_{\max}(T) = -0.0185T + 55.8 \tag{2.8}$$

By using equation 2.8, we can predict the maximum stress when the simulation temperature is given. However, this research only focuses on the mechanical properties of the hybrid materials in room temperature, therefore the simulation temperature of 300K was chosen.



Figure 2.18: Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the simulation temperature by using the system which contains 333, 396 atoms.

# 2.3.5 Strain Rate Effects

We now study the effects of strain rate on the mechanical properties of the material. The uni-axial tension test with different strain rate<sup>1</sup> was applied to the system. Then, the maximum stress, energy release and Young's modulus were calculated for each strain rate set up.

The results are shown in the Fig.2.19, it can be seen that when the strain rate decreases, the Young's modulus is convergence. This is because a lower strain rate means more time for the material to respond the loading [42], when the strain rate is small enough to let the material have enough time to respond the loading, then the stiffness of the material will have negligible change or even no change by continuous decreasing the strain rate. From the Fig.2.19 we can see that the strain rate has very small effects on the Young's modulus when it decreases from  $1.0 \times 10^{-3} picosecond^{-1}$  to  $1.0 \times 10^{-4} picosecond^{-1}$ . Therefore, the strain rate of  $1.0 \times 10^{-3} picosecond^{-1}$  was chosen to minimize the effects on the mechanical properties of the material.

 $<sup>\</sup>begin{array}{lll} {}^{1} \ 1.0 \ \times \ 10^{-4} picosecond^{-1}, 5.0 \ \times \ 10^{-4} picosecond^{-1}, 1.0 \ \times \ 10^{-3} picosecond^{-1}, 5.0 \ \times \ 10^{-3} picosecond^{-1}, 1.0 \ \times \ 10^{-2} picosecond^{-1}, 5.0 \ \times \ 10^{-2} picosecond^{-1}, 1.0 \ \times \ 10^{-1} picosecond^{-1}, 5.0 \ \times \ 10^{-1} picosecond^{-1}, 1.0 \ \times \ 10^{-1} picosecond^{-1} pi$ 



**Figure 2.19:** Simulation results on the maximum stress (fracture strength or  $\sigma_{\text{max}}$ ), energy released (*G*) and Young's modulus (*E*) as a function of the strain rate by using the system which contains 333, 396 atoms.
#### 2.3.6 Solid Thickness Effects

In Chapter 4, a set of geometrically identifiable hole configurations will be generated to investigate the toughness-strength correlation of the amorphous silica, and the xy plane of the solid needs to be large enough to spread out the configurations to prevent interplay between the holes. Therefore, an amorphous silicon dioxide structure which contains 1,008,000 atoms was created as shown in the Fig.2.20.



Figure 2.20: The ortho view of the structure which contains 1,008,000 SiO<sub>2</sub> atoms.

From the Fig.2.20, it can be seen that the thickness of the structure is much thinner than other systems we studied (see Fig.2.3) since by keeping the system size same, thickness reduction can increase the xy plane of the solid. And the style of

boundaries for the simulation box in z dimension is periodic, which means the simulation box can periodically repeat alone z direction. In other words, the thickness of the structure should have negligible effects on the mechanical properties of the solid. To study these effects, the uni-axial tension test was applied to the structure 1 which contains 333, 396 atoms and the structure 2 which contains 1,008,000 atoms (structure 1 was shown in the Fig.2.3 and structure 2 was shown in the Fig.2.20). Then, the maximum stress, energy release and Young's modulus were calculated to compare the mechanical properties of the 2 structures. Note that, the number of atoms in both structures are large enough to eliminate the size effects (see section 2.3.1). The results are shown in the Fig.2.21:

	Young's Modulus (Y)	Maximum Stress (σ <sub>xx</sub> )	Energy Release (J/m³)
Structure 1	78.85 Gpa	50.47 Gpa	15.0 J/m <sup>3</sup>
Structure 2	79.09 Gpa	49.82 Gpa	14.7 J/m <sup>3</sup>

Figure 2.21: Compare the mechanical properties between the structure 1 which contains 333, 396 atoms and the structure 2 which contains 1,008,000 atoms.

From the Fig.2.21, it can be seen that the mechanical properties of 2 structures are very similar. There are only 0.3%, 1.3% and 2.0% difference in Young's modulus, maximum stress and energy release between the structure 1 and structure 2. Therefore, the thickness effects on the mechanical properties of the solid can be neglected.

# 2.4 The Effects of Variables (System Size, Annealing Temperature, Strain Rate) on the Mechanical Properties of Amorphous Silicon Dioxide (ReaxFF Potential)

2.4.1 System Size Effects

In this section, we will study the effects of system size on the mechanical properties of amorphous silicon dioxide. Four amorphous silicon dioxide systems which contains 86,000, 345,000, 540,000 and 1,000,000 atoms were created by using the method introduced in section 2.1.3. The uni-axial tension tests were applied and then, the maximum stress, energy release and Young's modulus were calculated for each system. The results are shown in the Fig.2.22. From the results, we can see that, the maximum stress, energy released and Young's modulus are converging when the number of atoms in the system is increasing.

On the other hand, from the Fig.2.23, it can be seen that fracturing behavior of the system which contains 86,000 atoms is different compare to the systems which contains 345,000, 540,000 and 1,000,000 atoms, and this difference also can be seen from the Fig.2.24. For the system which contains 86,000 atoms, the material breaks into two pieces after fracturing which is shown in the Fig.2.24a1-a4. However, for the system which contains 540,000 atoms, multiple cracks are propagating during the failing of the material which is shown in the Fig.2.24b1-b4. This is because, with large system and domain size (for example 540,000 atoms), there is enough space to let multiple cracks spread out and nucleate in different locations. However, with small system and domain size (for example 86,000 atoms), there is insufficient



Figure 2.22: Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of system size.

space to nucleate multiple cracks. Therefore, to eliminate this kind of size effect, the system size should be larger than 345,000 atoms.



Figure 2.23: The stress vs strain curves for the amorphous silicon dioxide systems which contain 86,000, 345,000, 540,000 and 1,000,000 atoms.

### 2.4.2 Annealing Temperature Effects

To create an amorphous silicon dioxide structure, the thermal annealing method was applied to the system which was previously introduced in section 2.1.3. Through sudden increasing the temperature of the system to distort atom position and then, slowly cooling it back to room temperature, the amorphous structure is created. In this section, different annealing temperature was applied to the system (8,000K,



Figure 2.24: a1-a4. Sequence of snapshots of the system which contains 86,000 atoms is applied to the uni-axial tension test.b1-b4. Sequence of snapshots of the system which contains 540,000 atoms is applied to the uni-axial tension test.

10,000K, 12,000K) to investigate the effects of annealing temperature on the mechanical properties of material, and for each annealing temperature set up, the amorphous procedure (see section 2.1.3) and then the uni-axial tension test (see section 2.2) were applied to the system. After that, maximum stress, energy release and Young's modulus were calculated for each annealing temperature set up. The results are shown in the Fig.2.26.



**Figure 2.25:** The stress *vs* strain curves for the amorphous silicon dioxide system which contains 540,000 atoms with different annealing temperature(8,000K, 10,000K, 12,000K) applied.

From the Fig.2.26 and the stress vs strain curves shown in the Fig.2.25, it can be seen that the maximum stress and Young's modulus were decreasing by increasing the annealing temperature from 8,000K to 12,000K and these effects were



Figure 2.26: Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the annealing temperature by using the system which contains 540,000 atoms.

also verified in section 2.3.3 Fig.2.15 by using Tersoff potential. For the future study, 12,000K annealing temperature was chosen to consistent with Tersoff potential.

#### 2.4.3 Strain Rate Effects

In this section, we will study the effects of strain rate on the mechanical properties of amorphous silicon dioxide. The uni-axial tension test with different strain rate<sup>2</sup> was applied to the system. Then, the maximum stress, energy release and Young's modulus were calculated for each strain rate set up. The results are shown in the Fig.2.27.

From the Fig.2.27, it can be seen that when strain rate decreases, the maximum stress, energy release and Young's modulus decrease. This is because a lower strain rate can let material has more time to respond the loading [42] and which has also been verified in section 2.3.5 by using Tersoff potential.

From the Fig.2.28, we can see that when the uniaxnial tension test was applied with a strain rate of  $1.0 \times 10^{-6} femtosecond^{-1}$ , the stress vs strain curve we got is a typical stress vs strain curve for a brittle material. After the failure ,the stress in the material quickly drop to 0 Gpa, and which means the strain rate is low enough to let the material relax after the failure. However, for other cases, we can see that even a long time after the failure, there are still some residual stresses in those structures which means the strain rates for those cases are too high for the material to relax. Therefore, for the best results of silica, the strain rate of  $1.0 \times 10^{-6} femtosecond^{-1}$ will be consider for future study.

 $<sup>{}^2 \ 1.0 \</sup>times 10^{-6} femtosecond^{-1}, 5.0 \times 10^{-6} femtosecond^{-1}, 1.0 \times 10^{-5} femtosecond^{-1}, 5.0 \times 10^{-5} femtosecond^{-1}, 1.0 \times 10^{-4} femtosecond^{-1}$ 



Figure 2.27: Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the strain rate by using the system which contains 540,000 atoms.



Figure 2.28: The stress vs strain curves for the amorphous silicon dioxide system by applying different strain rate $(1.0 \times 10^{-6} femtosecond^{-1}, 5.0 \times 10^{-6} femtosecond^{-1}, 1.0 \times 10^{-5} femtosecond^{-1}, 5.0 \times 10^{-5} femtosecond^{-1}, 1.0 \times 10^{-4} femtosecond^{-1}).$ 

# 2.5 The Mechanical Properties of Amorphous Silicon Dioxide in Tersoff Potential

From section 2.3, we studied the effects of system size, dynamics equilibrium time-steps, annealing temperature, simulation temperature and strain rate on the mechanical properties of amorphous silicon dioxide. In collusion, the single crystalline silicon dioxide structure which contains 333,396 atoms was chosen to create the amorphous structure by using 90,000 dynamics equilibrium time-steps and 12,000K annealing temperature. After the amorphous procedure, the uni-axial tension test was applied to the system by using 300K simulation temperature and  $1.0 \times 10^{-3} picosecond^{-1}$  strain rate. The corresponding stress vs strain curve is shown in the Fig.2.29.



**Figure 2.29:** The stress vs strain curve and mechanical properties of amorphous silicon dioxide under uni-axial tension test at a strain rate of  $10^{-3}ps^{-1}$  (vacuum, 300K) by using Tersoff potential. And sequence of snapshots of stress ( $\sigma_{xx}$ ) distribution in amorphous silicon dioxide structure.

From the Fig.2.29, it can be seen that the simulation gave a value of 72.81 GPa for the Young's modulus which is in the range of experience values (from 69 GPa to 78.9 GPa)[31][43][44][45]. The simulation gave a value of 52.45 GPa for the maximum stress and the experience value is in the range of 11 - 14 GPa[31] which is not close to our result. However, Muralidharan, Simmons, Deymier and Runge [46] have already reported that under uni-axial strain test, the maximum stress for the amorphous silicon dioxide can be extraordinarily changed by using different potentials. For example, by using FG potential, the range of maximum stress is from 12GPa to 21GPa corresponding to the strain rate from  $0.05 picosecond^{-1}$  to  $0.5 picosecond^{-1}$ . However, by using S-potential, the range of maximum stress is from 24GPa to 35GPa corresponding to the strain rate from  $0.05 picosecond^{-1}$  to  $0.5 picosecond^{-1}$ [46]. Finally, the simulation gave a value of 15 J/m<sup>3</sup> for the energy release, this value will be a reference for the toughness calculation in the future.

### 2.6 The Mechanical Properties of Amorphous Silicon Dioxide in Reaxff Potential

From section 2.4, we studied the effects of system size, annealing temperature and strain rate on the mechanical properties of amorphous silicon dioxide. In conclusion, the single crystalline silicon dioxide structure which has 1 million atoms was chosen to create the amorphous structure by using 12,000K annealing temperature. After the amorphous procedure, the uni-axial tension test was applied to the system by using 300K simulation temperature and  $1.0 \times 10^{-6} femtosecond^{-1}$  strain rate. The corresponding stress vs strain curve is shown in the Fig.2.30.

From the Fig.2.30, it can be seen that the simulation gave a value of 71.59GPa



Figure 2.30: The stress vs strain curve and mechanical properties of amorphous silicon dioxide under uni-axial tension test at a strain rate of  $10^{-6}$  fs<sup>-1</sup> (vacuum, 300K) by using Reaxff potential.

for the Young's modulus which is in the range of experience values (from 69GPa to 78.9GPa)[31][43][44][45]. The simulation gave a value of 12.49GPa for the maximum stress and which is in the range of experience values (11 - 14GPa)[31]. This means Reaxff potential has a better prediction for the mechanical properties of Silica than Tersoff potential. Finally, the simulation gave a value of  $3.41 \text{ J/m}^3$  for the energy release, this value will be a reference for the toughness calculation in the future.

2.7 The Mechanical Properties of the Amorphous Silicon Dioxide Structure with Crack Existence (Tersoff)

### 2.7.1 The Amorphous Silicon Dioxide Structure with Crack Existence

We now study the mechanical properties of the amorphous silicon dioxide structure with crack existence. In this study, the certain area of the silicon dioxide structure was removed to create the crack. The final structure is shown in the Fig.2.31



Figure 2.31: (a)The amorphous silicon dioxide structure with crack existence. (b)The magnification of the crack.

From the Fig.2.31, it can be seen that there is a vacuum space between the



Figure 2.32: (a)The structure which dose not have vacuum space periodically repeat in the x direction. (b)The structure which has vacuum space periodically repeat in the x direction.

structure and the simulation box, and the width of the vacuum space should be enough to prevent the particles interacting across the boundary in the x direction. In our case, the particles can interact across the boundary in the x direction means the particles on the crack side can interact with the particles on the other side of the box in the x direction. In other worlds, the simulation box can periodically repeat alone the x direction as shown in the Fig.2.32. From the Fig.2.32(a), we can see that, without the vacuum space, the periodic repeating alone the x direction can convert the crack into a hole, and this is not the case we want to study. However, as shown in the Fig.2.32(b), if there has a vacuum space between the structure and the simulation box, when the stimulation box is periodically repeating alone the xdirection, since the vacuum space has already cut the interaction of the particles across the boundary in the x direction, therefore, the simulation box and each periodic image are isolated from each others and can not have any interaction with their neighborhoods in the x direction. This can let the crack show the right influence to the structure when the uni-axial tension is applied in the y direction.

### 2.7.2 The Vacuum Width Effecting the Mechanical Properties of the Material

From section 2.7.1, the vacuum space was introduced to prevent the particles interacting across the boundary in the x direction. In this section, the vacuum space with different width (from 10Å to 80Å) was applied to the system as shown in the Fig.2.33.

For each width set up, the uni-axial tension test was applied to the system in the y direction. However, the existence of the vacuum space leads to an issue which is the stress applied on the structure is underestimated during the uni-axial tension test. For example, when there is no vacuum space in the structure, the uniaxial tension applied on the structure is equal to the uni-axial tension applied on the simulation box. However, as shown in the Fig.2.34, when the structure has vacuum space, the uni-axial tension applied on the structure is larger than the uni-axial tension applied on the simulation box according to the equation of the uni-axial normal stress which is:

$$\sigma = \frac{F}{A} \tag{2.9}$$

where  $\sigma$  is the uni-axial normal stress, F is the force and A is the surface area. Then, based on the Fig.2.34, a equation is applied to the system to calculate the



**Figure 2.33:** Picture a - h corresponding to different vacuum width from  $10\mathring{A}$  to  $80\mathring{A}$ 

stress applied on the structure  $(\sigma_{yy1})$  by using the dependent variable which is the stress applied on the simulation box  $(\sigma_{yy2})$  and the equation is:

$$\sigma_{yy1} = \sigma_{yy2} \times \frac{L_x}{L_x - L_v} \tag{2.10}$$



Figure 2.34: When the force is applied on the xz-plane, the stress applied on the structure which has smaller area on the xz-plane is larger than the stress applied on the simulation box which has larger area on the xz-plane.

After the uni-axial tension test for each vacuum width set up, the maximum stress, energy release and Young's modulus were calculated. The results are shown in the Fig.2.35, it can be seen that, the vacuum width has very small effects on the maximum stress, energy release and Young's modulus. Therefore, the structure with 20 Å vacuum width was chosen.



**Figure 2.35:** Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the vacuum width.

# 2.7.3 The Mechanical Properties of the Amorphous Silicon Dioxide Structure with Crack Existence

From section 2.7.2, the structure with 20 Å vacuum width was chosen, then

the uni-axial tension test (see section 2.2) was applied to the system in the y direction, the results are shown in the Fig.2.36. It can be seen that, the energy release and maximum stress of the material with crack existence have a much lower value than the material without the crack and this is due to the stress concentration at the edge of the crack.



Figure 2.36: (a) The stress vs strain curves for the amorphous silicon dioxide with and without the crack existence. (b) The mechanical properties of the amorphous silicon dioxide with and without the crack existence.

From the Fig.2.37(b), it can be seen that when the uni-axial tension test was applying to the system, the stress was concentrating at the edge of the crack

(the crack nucleation). And when the stress is concentrating to a point which is higher than the fracture strength of the material, then the crack starts to grow as shown in the Fig.2.37(a1-a6). It can be seen that, the crack was propagating alone the x direction, this is because the stress was applying equally and contrarily in the y direction and this forces the crack to propagate horizontally. Besides, from the Fig.2.37(a4-a6), it can be seen that, the stress had a sudden decreasing (the color turn from red to green) when the crack was passing trough. This means the stress was released and the structure was relaxed after the passing of the crack.



Figure 2.37: (a1 - a6) Sequence of snapshots of the stress $(\sigma_{yy})$  distribution in the material when the uni-axial tension test was applying. (b) Before the failure of the material, the stress was concentrating at the edge of the crack when the uni-axial tension test was applying.

#### Chapter 3

### DEFORMATION AND FRACTURE MECHANICS OF A SINGLE-WALL CARBON NANOTUBE (SWCNT)

In molecular dynamics simulations, the mechanical properties of the carbon nanotube have been well studied. Yakobson et al. studied the nanotube behavior at high rate tensile strain by using Tersoff-Brenner's reactive empirical bond-order (REBO) potential[47]. Nath et al. studied and compared the nanomechanics of CNTs under tension by using different potentials[48]. Liew et al. studied the elastic and plastic properties of multi-walled carbon nanotubes under axial tension in molecular dynamics simulations[49]. However, all the studies of carbon nanotubes we mentioned above are either in axial direction or radius direction, the study for the mechanical properties of carbon nanotubes in lateral direction is lack, and which will be the main focus in this chapter.

In this chapter, we will study the basic structure properties about nanotubes. Then, in molecular dynamics simulations, the mechanical properties and fracture mechanism of a carbon nanotube in axial direction and lateral direction are studied by using AIREBO potential.

#### 3.1 The Method to Create a Single-Wall Carbon Nanotube (SWCNT)

The carbon nanotube is a carbon made, tube-shaped material and has the radius in nanometer scale. The structure of a SWCNT can be made by warping one layer of a graphene sheet. The way graphene is wrapped is represented by a pair of indices (n, m) as shown in the Fig.3.1 (In the future, SWCNT or single-wall carbon nanotube will be represented by CNT or carbon nanotube for convenience),



Figure 3.1: The way graphene is wrapped is decided by the vector  $C_h$  which is represented by a pair of indices (n, m). T is the tube axis,  $a_1$  and  $a_2$  are the unit vectors of the graphene sheet [50].

From the Fig.3.1, the representation of  $C_h$  is shown below:

$$C_h = na_1 + ma_2 \tag{3.1}$$

From Equation 3.1, it can be seen that, by changing n and m which are the number of unit vectors  $a_1$  and  $a_2$ , we can adjust the length and direction of the vector  $C_h$ . If m = 0, then

$$C_h = na_1 \tag{3.2}$$

This means the nanotube will be made by wrapping the graphene sheet in the  $a_1$  direction, and this kind of nanotube is called zigzag nanotube (see Fig.3.2(b)). If m = n, then:

$$C_h = n(a_1 + a_2) \tag{3.3}$$

This means the nanotube will be made by wrapping the graphene sheet in the  $a_1 + a_2$  direction, and this kind of nanotube is called armchair nanotube(see Fig.3.2(a)). The diameter of a nanotube can be calculated by using following equation:

$$d = \frac{a}{\pi}\sqrt{(n^2 + nm + m^2)}$$
(3.4)

where a = 0.246 nm. For example if (n, m) = (20, 20) the diameter of the nanotube is:

$$d = \frac{0.246}{\pi}\sqrt{(20^2 + 20 \times 20 + 20^2)} = 2.7nm \tag{3.5}$$

Therefore, a carbon nanotube with (n, m) = (20, 20) is formed for the deformation and fracture studies.

### 3.2 Applying Uni-axial Tension Test to the Carbon Nanotube

After creating the nanotube structure, the uni-axial tension test is ready to apply to the system. Before the deformation, the external stress tensor is applied



Figure 3.2: (a) The graphene nanoribbon wrapped in armchair direction to form an armchair nanotube. (b) The graphene nanoribbon wrapped in zigzag direction to form a zigzag nanotube.

to the simulation box (static equilibrium) to reach both the potential energy minimization and the equally between system pressure tensor and the specified external tensor[27](see section1.2.1). After that, the uni-axial tension test is applied to the system by using *fix deform* command (see section 1.2.5 and 2.2). During the deformation, *fix nvt* command is carried out to the system, to make sure the number of atoms, the volume of the system and the temperature of the system are keep as constants (see section 1.2.3). And the strain rate of  $1.0 \times 10^{-3}$  ps and 1K simulation temperature are considered during the deformation. The tension test results of the carbon nanotube will be introduced in section 3.3.

# 3.2.1 Calculate the Axial Stress Applied on a Nanotube During the Uniaxial Tension Test

From the Fig.3.3, we can see that when the uni-axial tension test is applied along the axial direction (z direction) of a nanotube, the stress applied on the simulation box (P) is much smaller than the stress applied on the nanotube ( $\sigma_{zz}$ ) since the surface area of the nanotube on the xy plane is much smaller than the surface area of the simulation box on the xy plane (see section 2.7.2).

In order to abstract the actual stress applied on the nanotube, we have to transfer the stress acting on the simulation box to the stress acting on the nanotube. Since the applied force is area independent, then we have:

$$F = P \times A = \sigma_{zz} \times A_{CNT} \tag{3.6}$$

In which, F is the force applied to the system, P is the pressure tensor in the z direction, A is the surface area of the simulation box on the xy plane,  $\sigma_{zz}$  is the



Figure 3.3: The top and front views of a nanotube, in which P is the pressure tensor on z direction,  $L_x$  and  $L_y$  are box length on x and y directions.

stress acting on the nanotube and  $A_{CNT}$  is the surface area of the nanotube on the xy plane. Then we have:

$$A = L_x \times L_y$$

$$A_{CNT} = \pi \times d \times t$$
(3.7)

 $L_x$  and  $L_y$  are box length on x and y directions, d is the diameter of the nanotube and t is the thickness of the nanotube. Finally, we substitute equation 3.7 into equation

3.6, then the stress applied on the nanotube is equal to:

$$\sigma_{zz} = \frac{P \times L_x \times L_y}{\pi \times d \times t} \tag{3.8}$$

# 3.2.2 Calculate the Lateral Stress Applied on a Nanotube During the Uni-axial Tension Test

The idea of calculating the lateral stress applied on the nanotube is similar to the nanotube axial stress calculation (see section 3.2.1). From the Fig.3.4, we can see that the lateral stress only acting on the edges of the nanotube where are the area A and B. Based on that, we can transfer the pressure tensor P in y direction to the nanotube lateral stress  $\sigma_{yy}$ .

Since the applied force is area independent, we have:

$$F = P \times A = \sigma_{uu} \times A_{CNT} \tag{3.9}$$

In which, F is the force applied to the system, P is the pressure tensor in y direction, A is the surface area of the simulation box on the xz plane,  $\sigma_{yy}$  is the lateral stress acting on the nanotube and  $A_{CNT}$  is the surface area of A and B. Then we have:

$$A = L_x \times L_z$$

$$A_{CNT} = 2 \times L_z \times t$$
(3.10)

 $L_x$  and  $L_z$  are box length on x and z directions and t is the thickness of the nanotube. Finally, we substitute equation 3.10 into equation 3.9, then the lateral stress applied on the nanotube is equal to:

$$\sigma_{yy} = \frac{P \times L_x \times L_z}{2 \times L_z \times t} = \frac{P \times L_x}{2 \times t}$$
(3.11)



Figure 3.4: The top and right views of a nanotube, in which P is the pressure tensor in y direction,  $L_x$ ,  $L_y$  and  $L_z$  are box length on x, y and z directions,  $\sigma_{yy}$  is the nanotube lateral stress.

### 3.3 The Mechanical Properties of a Single-Wall Carbon Nanotube (SWCNT) in AIREBO Potential

### 3.3.1 The Mechanical Properties of a Single-Wall Carbon Nanotube (SWCNT) in the Axial Direction

From the section 3.1, an armchair carbon nanotube with (n, m) = (20, 20)(d = 2.7 nm) was formed. By using this nanotube with AIREBO potential (see section 1.3.3), uni-axial tension test in the axial direction was applied to the system (see section 3.2). The results are shown in the Fig.3.5.



Figure 3.5: (a) The stress vs strain curve for an armchair carbon nanotube with  $(n,m) = (20,20) \ (d = 2.7 \text{ nm})$  under uni-axial tension test at a strain rate of  $10^{-3} \text{ ps}^{-1}$  (vacuum, 1K) (b) The mechanical properties of the carbon nanotube.

From the Fig.3.5, we can see that the simulation gave a value of 836.83GPa for

the Young's Modulus which is close to the range of experience values 1.3 - 0.4/+0.6 TPa (depending on tube chirality) reported by Krishnan et al.[9]. And the maximum strength we got from the simulation is 119.12GPa which is in the range of theoretical calculation prediction of tensile strength 75 - 135GPa (depending on tube chirality) for an ideal single-walled carbon nanotube (SWNT)[8].



Figure 3.6: A sequence of snapshots of stress  $(\sigma_{zz})$  distribution in an armchair carbon nanotube with (n, m) = (20, 20) (d = 2.7 nm) during the uni-axial tension test on the axial direction.

From the Fig.3.6, it can be seen that when the stress reaches the maximum strength which is 119.12GPa, one bond is broken leads to one hole, as shown in the Fig.3.6(A). As strain increases, more bonds are broken and the cracks propagate alone both zigzag and armchair directions until the total fracture (Fig.3.6(B)-(F)). This kind of brittle fracture process has already been reported by K.M. Liew [49] who studied the elastic and plastic properties of multi-walled carbon nanotubes under axial tension by using second-generation of reactive empirical bond-order (REBO) potential coupled with the Lennard-Jones potential.

# 3.3.2 The Mechanical Properties of a Single-Wall Carbon Nanotube (SWCNT) in the Lateral Direction

In this section, we will study the mechanical properties of a nanotube in the lateral direction. An armchair carbon nanotube with (n, m) = (20, 20) (d = 2.7 nm) introduced in the section 3.3.1 was used to study this problem. Then, by using this nanotube with AIREBO potential (see section 1.3.3), the uni-axial tension test in the lateral direction (y direction) was applied to the system (see section 3.2). The results are shown in the Fig.3.7.



Figure 3.7: (a) The stress vs strain curve for an armchair carbon nanotube with  $(n,m) = (20,20) \ (d = 2.7 \text{nm})$  under uni-axial tension test in the lateral direction at a strain rate of  $10^{-3} \text{ ps}^{-1}$  (vacuum, 1K) (b) The mechanical properties of the carbon nanotube in lateral direction.



Figure 3.8: A sequence of snapshots of stress  $(\sigma_{yy})$  distribution in an armchair carbon nanotube with (n,m) = (20,20) (d = 2.7nm) during the uni-axial tension test on the lateral direction.

From the Fig.3.7 we can see that, the mechanical properties of the nanotube in lateral direction are much lower than its axial direction. From the Fig.3.8, we can see the stress ( $\sigma_{yy}$ ) distribution in the armchair carbon nanotube during the uni-axial tension test, and in Fig.3.8(B)-(E) we can clearly see that the stress is concentrated on the yz face of the nanotube and finally fractured at the middle of the yz face of the nanotube.

### Chapter 4

### CRACK PROPAGATION IN CNT-SIO<sub>2</sub> NANOCOMPOSITES

In this chapter, we insert a carbon nanotube into the silica matrix to assembly the CNT-silica nanocomposite. By applying density function theory(DFT) to the CNT-silica system, the cnt-silica interfacial environment has been fully studied. Then by changing the nanotube radius and interfacial cohesive strength between the carbon nanotube and silica, we can understand how the nanotube radius and interfacial cohesive strength effect the mechanical properties such as maximum strength, toughness and Young's modulus of the CNT-silica nanocomposite. All the studies will use both Tersoff and Reaxff potential to validate the results.

### 4.1 Interfacial Strength

To define the interfacial interaction between the nanotube and the silica matrix, hybrid potential with Lennard-Jones (LJ) form is used. By using hybrid style, exactly one pair style is assigned to each pair of atom types. For example, by using the hybrid style to simulate the interfacial interaction between the nanotube and the silica matrix, the Si atoms and O atoms interact with each other via the Tersoff potential (see section 1.3.1), the C atoms interact with each other via the AIREBO potential (see section 1.3.3) and the silica/CNT surface interaction is computed via
a lj/cut potential. To determine the parameters charactering of lj/cut potential to represent the interfacial interaction between the nanotube and the silica matrix, the density functional theory (DFT) simulation as implemented in the SIESTA code is carried out. First, an amorphous silica with 324 atoms is prepared by using the LAMMPS simulation in three steps. First, *fix nvt* (see section 1.2.3) is applied to the system to melt the system under 8000K temperature, second *fix nve* (see section 1.2.4) is applied to anneal the system to 1K, and third, statically relaxing the structure by applying the external stress tensor to the simulation box to reach the minimization of the potential energy (see section 1.2.1). The amorphous structure is shown in the Fig.4.1:



Figure 4.1: Site-dependent electronic interaction between SiO<sub>2</sub> and CNT. The weakest interaction is identified at  $x_0 = 18.25$ Å, and the strongest interaction is identified at  $x_0 = 8.25$ Å. For all the cases, the LJ-parameters representing the two-body interaction are kept fixed to  $\sigma = 3.0$  and  $\epsilon = 0.050$  eV. The nanotube diameter is 7.52Å and its length is 16.32Å.

The LJ potential is mathematically represented by following equation:

$$V = 4\epsilon \left( \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12} \right) \tag{4.1}$$

Where  $\epsilon$  is the depth of the potential well,  $\sigma$  is the distance where the inter-particle potential is 0, r is the distance between the particles. To determine the parameters charactering of the interfacial interaction between the nanotube and the silica matrix, we place a nanotube on the silica matrix, then by changing the separation distance between the nanotube and silica matrix, the energy of the whole system is recorded, and the graph of strength versus distance for the Lennard-Jones potential is generated. However, in our case, for the aSiO2-CNT system, a unique choice of the LJ parameters ceases to exist, since the interaction between CNT and  $SiO_2$ highly depends on the atomistic details of the interface. In order to investigate the site effect, the nanotube is placed at the silica surface with different location alone the x direction, then the strength versus separation distance for the Lennard-Jones potential at different location is recorded. The results are shown in the Fig.4.1. From the Fig.4.1, we can see that the weakest interaction is at  $x_0 = 18.25$ Å, and the strongest interaction is at  $x_0 = 8.25$ Å. The binding strength varies from 0.375 to 0.566 eV/Å. Therefore, a range of binding strength have to be considered to explore their influence to the mechanical properties of  $CNT-SiO_2$  nanocomposites.

## 4.2 The Fracture Mechanism of the CNT-SiO<sub>2</sub> Nanocomposite and the Silica Structure with a Hole (Tersoff Potential)

In this section, we will study the fracture mechanism of the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole. The CNT-SiO<sub>2</sub> nanocomposite is assembled by inserting the nanotube into the silica matrix with 0.05ev cohesive strength as shown in the Fig.4.2.



Figure 4.2: (a) The top view of the CNT-SiO<sub>2</sub> nanocomposite with  $L_x = 1028$ Å,  $L_y = 849$ Å,  $L_z = 16.3201$ Å, d = 178Å,  $l_c = 100$ Å and  $l_n = 100$ Å. (b) The front view of the CNT-SiO<sub>2</sub> nanocomposite. (c) The ortho view of the nanotube inserting into the silica matrix.

From the Fig.4.2 we can see that the length of the CNT-SiO<sub>2</sub> nanocomposite  $(L_x)$  is equal to 1028Å, the width of the CNT-SiO<sub>2</sub> nanocomposite  $(L_y)$  is equal to 849Å and the thickness of the CNT-SiO<sub>2</sub> nanocomposite  $(L_z)$  is equal to 16.3201Å.

The diameter of the nanotube (d) is equal to 178Å, the distance from the crack tip to the edge of the nanotube  $(l_n)$  is equal to 100Å and the crack length  $(l_c)$  is equal to 100Å. On the other hand, the silica structure with a hole is also built as shown in the Fig.4.3.



Figure 4.3: (a) The ortho view of the CNT-SiO<sub>2</sub> nanocomposite and enlarged picture of the nanotube assembled in the silica matrix. (b) The ortho view of the silica structure with a hole and enlarged picture of the hole in the silica matrix.

From the Fig.4.3, it can be seen that in silica structure, the diameter of the hole is equal to the diameter of the nanotube in the CNT-SiO<sub>2</sub> nanocomposite and the other dimensions such as  $L_x$ ,  $L_y$ ,  $L_z$ ,  $l_n$  and  $l_c$  for both CNT-SiO<sub>2</sub> nanocomposite and silica structure are also identical. Then the uni-axial tension tests (see section 2.2) are applied to the CNT-SiO<sub>2</sub> nanocomposite and silica structure, the results are shown in the Fig.4.4.

From the Fig.4.4, we can see that before the deformation, the structure is free of stress which is shown in the Fig.4.4 (a1) and (a2). Then during the deformation, the stress starts to nucleate at the crack tip and the local stress around the crack tip is gradually increased as shown in the Fig.4.4 (b1) and (b2). Until the local stress at the crack tip is higher than the fracture strength of the silica, then the crack starts to grow as shown in the Fig.4.4 (c1) and (c2). Since the presenting of the hole or nanotube stopped the crack growing, the stress starts to nuclear at the right edge of the hole or nanotube as shown in the Fig.4.4 (d1) and (d2). When the local stress at the right edge of the hole or nanotube is higher than the fracture strength of the silica, the crack starts to nuclear and grow at the right edge as shown in the Fig.4.4 (e1) and (e2). Finally the structure is totally failed and the stress is released as shown in the Fig.4.4 (f1) and (f2).

From the Fig.4.4, we can see that the stress vs strain curves for both CNT-SiO<sub>2</sub> nanocomposite and silica structure with a hole have two peaks. First peak is when the structure starts to fail and the second peak is when the crack nucleated and starts to grow at the edge of the hole or nanotube. Therefore, in the future study, the results will be separated into two parts as shown in the Fig.4.5. The first part will include the results of  $\sigma_{max1}$ ,  $G_{c1}$ , and E. The second part will include the results of  $\sigma_{max2}$  and  $G_{c2}$ .

## 4.3 The Fracture Mechanism of the CNT-SiO<sub>2</sub> Nanocomposite and the Silica Structure with a Hole (Reaxff Potential)

In this section, we will study the fracture mechanism of the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole by using the reaxff potential. The CNT-SiO<sub>2</sub> nanocomposite is assembled by inserting the nanotube into the silica matrix with 0.05ev cohesive strength as shown in the Fig.4.2 and the silica structure with a hole is also built as shown in the Fig.4.3. The dimensions and other details of the nanocomposite and silica structure were previously introduced in the section 4.2. Then the uni-axial tension tests (see section 2.2) are applied to the CNT-SiO<sub>2</sub> nanocomposite and silica structure, the results are shown in the Fig.4.6.

From the Fig.4.6, we can see that before the deformation, the structure is free of stress which is shown in the Fig.4.6 (a1) and (a2). Then during the deformation, the stress starts to nucleate at the crack tip and the local stress around the crack tip is gradually increased as shown in the Fig.4.6 (b1) and (b2). Until the local stress at the crack tip is higher than the fracture strength of the silica, then the crack starts to grow as shown in the Fig.4.6 (c1) and (c2). Since the presenting of the hole or nanotube stopped the crack growing, the stress starts to nuclear at the right edge of the hole or nanotube as shown in the Fig.4.6 (d1) and (d2). When the local stress at the right edge of the hole or nanotube is higher than the fracture strength of the silica, the crack starts to nuclear and grow at the right edge as shown in the Fig.4.6 (e1) and (e2). Finally the structure is totally failed and the stress is released as shown in the Fig.4.6 (f1) and (f2).

#### 4.4 The Cohesive Strength Effects (Tersoff Potential)

In this section, we will study how the cohesive strength between the silica matrix and CNT effects the mechanical properties of CNT-SiO<sub>2</sub> nanocomposite. The CNT-SiO<sub>2</sub> nanocomposite is assembled by inserting the nanotube into the silica matrix with a set of cohesive strength<sup>1</sup> and the silica structure with a hole is also built to compare with the CNT-SiO<sub>2</sub> nanocomposite results. The dimensions and other details of the nanocomposite and the silica structure are shown in the Fig.4.2 and Fig.4.3. Then, the uni-axial tension tests (see section 2.2) are applied to the system. After that, the maximum stress, energy release and Young's modulus are calculated for each cohesive strength set up. The results are shown in the Fig.4.7, 4.8 and 4.9.

From the Fig.4.7 (the first peak results, see Fig.4.5), we can see that, in the range of 0.005ev to 0.05ev, the cohesive strength dose not have significant effects on the  $\sigma_{\text{max1}}$  and  $G_{c1}$ . In the range of 0.05ev to 0.1ev, there is a sharp increase for the  $\sigma_{\text{max1}}$  and  $G_{c1}$ . From 0.05ev to 0.1ev, the values of  $\sigma_{\text{max1}}$  increase from 14.756GPa to 15.923GPa and the values of  $G_{c1}$  increase from 1.246 J/m<sup>3</sup> to 1.268 J/m<sup>3</sup>. After that, in the range of 0.1ev to 0.35ev, the  $\sigma_{\text{max1}}$  and  $G_{c1}$  are gradually increased. Then, in

<sup>&</sup>lt;sup>1</sup> 0.005ev, 0.01ev, 0.05ev, 0.1ev, 0.15ev, 0.2ev, 0.25ev, 0.3ev, 0.35ev

order to compare the mechanical properties between the  $\text{CNT-SiO}_2$  nanocomposite and silica structure with a hole, the following equation is used:

Relative change
$$(x, x_{\text{reference}}) = \frac{\text{Actual change}}{x_{\text{reference}}} = \frac{\Delta}{x_{\text{reference}}} = \frac{x - x_{\text{reference}}}{x_{\text{reference}}}$$
 (4.2)

For example, we want to compare the  $\sigma_{max1}$  between the CNT-SiO<sub>2</sub> nanocomposite and silica structure with a hole, then the equation 4.2 becomes:

Relative change(
$$\sigma_{\max 1}^{cnt \ silica}, \sigma_{\max 1}^{silica}$$
) =  $\frac{\sigma_{\max 1}^{cnt \ silica} - \sigma_{\max 1}^{silica}}{\sigma_{\max 1}^{silica}}$  (4.3)

By applying the equation 4.2, the relative differences between the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole are shown in the Fig.4.9.

From the Fig.4.9 we can see that in the range of 0.005ev to 0.05ev, the relative difference of the  $\sigma_{\text{max1}}$  is below 0.4% and the relative difference of  $G_{c1}$  is below 2%. However, in the range of 0.05ev to 0.1ev, the relative difference of  $\sigma_{\text{max1}}$  suddenly increased to 7.5%. And the relative difference of  $G_{c1}$  also increased to 14.5%. To investigate the reasons behind that, the atomic structures of the CNT-SiO<sub>2</sub> nanocomposite during the deformation are plotted as shown in the Fig.4.10.

From the Fig.4.10(a2), we can see that, when the cohesive strength is at 0.05ev, the nanotube is delaminated before the crack starts to grow. However, when the cohesive strength is at 0.1ev, the nanotube delamination didn't happen. In the Fig.4.10(b3), the crack starts to grow and encounter with the nanotube, then in the Fig.4.10(b4), the nanotube is failed and stress on the nanotube is released. When the cohesive strength is at 0.05ev, since the nanotube delamination happened before the crack propagation and the nanotube can not absorb energy anymore after the

delamination. Therefore, all the energy will be absorbed by the silica matrix after the nanotube delamination, which is the same situation when deforming the silica structure with a hole. And that is why when the nanotube delamination happened before the crack propagation, the values of  $\sigma_{max1}$  and  $G_{c1}$  are almost same compare to the silica structure with a hole. However, if the nanotube delamination didn't happen, the energy will be absorbed by both silica matrix and nanotube, which means the CNT-SiO<sub>2</sub> nanocomposite can absorb more energy than the situation which the nanotube delamination is happened. Therefore, that is why in the range of 0.05ev to 0.1ev, there is a sharp increasing for the  $\sigma_{max1}$  and  $G_{c1}$ . Before the increasing, during the deformation, the nanotube delamination happened, and after the increasing, the nanotube delamination didn't happen.

For the second peak results which are shown in the Fig.4.7(b1), we can not see any obvious relationships between the cohesive strength and  $\sigma_{max2}$ ,  $G_{c2}$ . Since the crack nucleation at the interface of the CNT and silica matrix depends on many factors such as cohesive strength, local atomic structure and stress distribution of the silica matrix around the area of the crack nucleation and the stress distribution on the nanotube, therefore it is very hard to find a relationship between the cohesive strength and  $\sigma_{max2}$ ,  $G_{c2}$ .

From the results showing above, we can have a clear idea how the cohesive strength effects the mechanical properties of  $CNT-SiO_2$  nanocomposite, and how to design the interface between the CNT and silica matrix to maximum the mechanical properties of  $CNT-SiO_2$  nanocomposite.

#### 4.5 The Cohesive Strength Effects (Reaxff Potential)

In this section, we will study how the cohesive strength between the silica matrix and CNT effects the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite in Reaxff potential. The CNT-SiO<sub>2</sub> nanocomposite is assembled by inserting the nanotube into the silica matrix with a set of cohesive strength<sup>2</sup> and the silica structure with a hole is also built to compare with the CNT-SiO<sub>2</sub> nanocomposite results. The dimensions and other details of the nanocomposite and the silica structure are shown in the Fig.4.2 and Fig.4.3. Then, the uni-axial tension tests (see section 2.2) are applied to the system. After that, the maximum stress, energy release and Young's modulus are calculated for each cohesive strength set up. The results are shown in the Fig.4.11, 4.12 and 4.13.

From the Fig.4.11(a1) and (a2), we can see that when the cohesive strength increases, the maximum stress ( $\sigma_{max1}$ ) and energy released ( $G_{c1}$ ) also increase. The higher cohesive strength means the higher bonding strength between the Si-C and O-C. When deforming the CNT-SiO<sub>2</sub> nanocomposite, the force acting on the nanotube is applied by the silica matrix through the interface. When cohesive strength is weak, such as at 0.005ev, 0.01ev and 0.05ev, the nanotube delamination happened during the deformation (see Fig.4.14(a2) and (b4)). Since during the deformation, the nanotube can not absorb energy anymore and all the energy will be absorbed by the silica matrix after the nanotube delamination. In order to increase the capacity of the CNT-SiO<sub>2</sub> nanocomposite for observing the deforming energy, delaying the timing of the delamination is necessary which can be implemented by increasing

<sup>&</sup>lt;sup>2</sup> 0.005ev, 0.01ev, 0.05ev, 0.1ev, 0.15ev

the cohesive strength. This analysis can be proved from the Fig.4.14 and 4.11. In the Fig.4.14, we can see that when the cohesive strength is at 0.005ev and strain is at 0.01940, the nanotube delamination is happened. When the cohesive strength increases from the 0.005ev to 0.05ev, then the strain of delamination also increases from 0.01940 to 0.10420. From the Fig.4.11(a1) and (a2), we can see that when the cohesive strength increases from the 0.005ev to 0.05ev, the  $\sigma_{\text{max1}}$  increases from 4.350GPa to 5.215GPa, and  $G_{c1}$  increases from 0.244J/m<sup>3</sup> to 0.349J/m<sup>3</sup>.

In the Fig.4.15, we can see that when the cohesive strength is at 0.1ev, the nanotube delamination didn't happen. In the Fig.4.15(a3), the crack starts to grow and encounter with the nanotube, then in the Fig.4.15(a4), the nanotube is failed and stress on the nanotube is released. Since in this case the cohesive strength is strong enough to prevent the nanotube delamination. Therefore, the energy will be absorbed by both silica matrix and nanotube, which means the CNT-SiO<sub>2</sub> nanocomposite can absorb more energy than the case which the delamination is happened. Compare to the silica structure with a hole, we can conclude that the presenting of the nanotube has a positive effect on  $\sigma_{\text{max1}}$  and  $G_{c1}$ . In the Fig.4.13(a1) and (a2), when cohesive strength is at 0.15ev, the relative difference of the  $\sigma_{\text{max1}}$  is above 35% and the relative difference of  $G_{c1}$  is above 72%.

According to the power law, we can fit the MD data points to a curve to represent the relationship between the cohesive strength and the maximum stress  $(\sigma_{\text{max1}})$  and the relationship between the cohesive strength and the toughness  $(G_{c1})$ .

The functions of the fitted curves are shown below:

$$\sigma_{\max 1}(x) = 2.96 + 4.222 \times x^{0.2061} \tag{4.4}$$

$$G_{c1}(x) = -0.3311 + 0.8349 \times x^{0.0691} \tag{4.5}$$

By using these mathematical representations, we not only can predict the  $\sigma_{\text{max1}}$  and  $G_{c1}$  of the CNT-SiO<sub>2</sub> nanocomposite by a given cohesive strength, but also can guide us to engineer the interface of the CNT and silica matrix to optimal the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite. In the Fig.4.11(b1), we can see that when the cohesive strength increases, the values of  $\sigma_{\text{max2}}$  are around 4.9GPa, which means the cohesive strength does not have significant effects on the  $\sigma_{\text{max2}}$ . Since second crack is nucleated after the nanotube delamination or failure. Therefore, the  $\sigma_{\text{max2}}$  will only depend on the atomic structure and stress field on the silica matrix and not depend on the cohesive strength of the interface.

#### 4.6 The Radius Effects (Tersoff Potential)

In this section, we will study how the radius of the nanotube effects the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite. The CNT-SiO<sub>2</sub> nanocomposite is assembled by inserting the nanotube into the silica matrix with different radius (see table 4.1) and the silica structure with the same radius set up is also built to compare with the CNT-SiO<sub>2</sub> nanocomposite results. Here are few examples in the Fig.4.16. From the Fig.4.16, we can see that the  $L_x$ ,  $L_y$ ,  $L_z$ ,  $l_n$  and  $l_c$  for these CNT-SiO<sub>2</sub> nanocomposites are identical compare to the structure we studied in the section 4.2 (see Fig.4.2 and Fig.4.3) and the only differences in these structures are the radius of the nanotube.

Area Fraction of the	
Nanotube in Domain (%)	Radius of the Nanotube (Å)
0.5	36.179532
1.0	51.575077
1.5	63.121736
2.0	72.743952
2.5	81.211502
3.0	88.909275
3.5	96.222159
4.0	102.765266
4.5	108.923484
5.0	115.081702
5.5	120.470143
6.0	125.858584
6.5	130.862136
7.0	135.865689
7.5	140.869241
8.0	145.487905
8.5	149.721680
9.0	154.340343
9.5	158.574118
10	162.423005

 Table 4.1: The area fraction of the nanotube in domain and its corresponding radius.

Then, the uni-axial tension tests (see section 2.2) are applied to the system. After that, the maximum stress, energy release and Young's modulus are calculated for each nanotube (hole) radius set up. The results are shown in the Fig.4.17, 4.18 and 4.19. From the Fig.4.17(a1), we can see that when the area fraction of the nanotube increases from the 0.5% to 3.0% and from the 3.5% to 10%, the maximum stress  $(\sigma_{max1})$ , energy released  $(G_{c1})$  and Young's modulus (E) are linearly decreased. This is because the increase of the area fraction of the nanotube leads to the material in the CNT-SiO<sub>2</sub> nanocomposite decreases which means the capacity of the CNT-SiO<sub>2</sub> nanocomposite for observing the deforming energy will be decreased. This will make the material fracture earlier and less stiff. Another point we want to make from the Fig.4.17(a1) is that, in the range from 3.0% to 3.5%, there is a sharp increase for the  $\sigma_{max1}$  and  $G_{c1}$ . From the 3.0% to 3.5%, the values of  $\sigma_{max1}$  increase from 14.756GPa to 15.580GPa and the values of  $G_{c1}$  increase from 1.268 J/m<sup>3</sup> to 1.378J/m<sup>3</sup>.

By applying the equation 4.2, the relative differences between the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole are shown in the Fig.4.19. From the Fig.4.19(a3) we can see that in the range of 0.5% to 3.0%, the relative difference of the  $\sigma_{max1}$  is below 1.6% and the relative difference of  $G_{c1}$  is below 2.0%. However, in the range of 3.0% to 3.5%, the relative difference of  $\sigma_{max1}$  suddenly increased to 7.3%. And the relative difference of  $G_{c1}$  also increased to 13.1%. To investigate the reasons behind that, during the deformation, the atomic structures of the CNT-SiO<sub>2</sub> nanocomposites with 3.0% and 3.5% nanotube area fraction are plotted as shown in the Fig.4.20.

From the Fig.4.20(a2), we can see that, when the area fraction of the nanotube is at 3.0%, the nanotube is delaminated before the crack propagation. However, when the area fraction of the nanotube is at 3.5%, the nanotube is delaminated after the crack starts to grow. In the Fig.4.20(b3), the crack starts to grow, then before encountering with the nanotube, shown in the Fig.4.20(b4), the nanotube is delaminated and stress on the nanotube is released. When the area fraction of the nanotube is at 3.0%, since the nanotube delamination is before the crack propagation and the nanotube can not absorb energy anymore after the delamination. Therefore, all the energy will be absorbed by the silica matrix after the delamination, which is the same situation when deforming the silica structure with a hole. And that is why if the nanotube delamination happened before the crack propagation, the values of  $\sigma_{\text{max1}}$  and  $G_{c1}$  are almost same compare to the silica structure with a hole (see Fig.4.19). However, if the nanotube delamination happened after the crack starts to grow, during the crack nucleation, the energy will be absorbed by both silica matrix and nanotube which means the CNT-SiO<sub>2</sub> nanocomposite can absorb more energy than the situation which the nanotube delamination happened before the crack propagation. Therefore, that is why in the range of 3.0% to 3.5%, there is a sharp increase for the  $\sigma_{\text{max1}}$  and  $G_{c1}$ . Before the increase, the nanotube delamination is before the crack propagation, and after the increase, the nanotube delamination is after the crack starts to grow or the delamination didn't happen at all.

For the second peak results which are shown in the Fig.4.17(b1), we can not see any obvious relationships between the nanotube area fraction and  $\sigma_{max2}$ ,  $G_{c2}$ . Since the crack nucleation at the interface depends on many factors such as the cohesive strength, the local atomic structure of the silica matrix and stress distribution at the area of the crack nucleation and the stress distribution on the nanotube. Therefore, it is very hard to find a relationship between the nanotube area fraction and the  $\sigma_{max2}$ ,  $G_{c2}$ .

From the results showing above, we can have an idea about how the radius of the nanotube effects the mechanical properties of  $CNT-SiO_2$  nanocomposite, and how to design the nanotube to maximum the mechanical properties of  $CNT-SiO_2$  nanocomposite.



Figure 4.4: 1. The stress vs strain curve of the CNT-SiO<sub>2</sub> nanocomposite with cohesive strength of 0.05ev under uni-axial tension test at a strain rate of  $2.0 \times 10^{-4} \text{ ps}^{-1}$  (vacuum, 1K) by using Tersoff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite (a1-f1). 2. The stress vs strain curve of the silica structure with a hole under uni-axial tension test at a strain rate of  $10^{-3} \text{ ps}^{-1}$  (vacuum, 1K) by using Tersoff potential. And sequence is strain to the silica structure with a hole under uni-axial tension test at a strain rate of  $10^{-3} \text{ ps}^{-1}$  (vacuum, 1K) by using Tersoff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in the silica structure (a2-f2).



Figure 4.5: A typical stress vs strain curve for the CNT-SiO<sub>2</sub> nanocomposite or the silica structure with a hole.



Figure 4.6: 1. The stress vs strain curve of the CNT-SiO<sub>2</sub> nanocomposite with cohesive strength of 0.05ev under uni-axial tension test at a strain rate of  $10^{-3}$  ps<sup>-1</sup> (vacuum, 300K) by using Reaxff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite (a1-f1). 2. The stress vs strain curve of the silica structure with a hole under uni-axial tension test at a strain rate of  $10^{-3}$  ps<sup>-1</sup> (vacuum, 300K) by using Reaxff potential. And sequence of snapshots of stress vs strain curve of the silica structure with a hole under uni-axial tension test at a strain rate of  $10^{-3}$ ps<sup>-1</sup> (vacuum, 300K) by using Reaxff potential. And sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in the silica structure (a2-f2).



Figure 4.7: (a1) The first peak simulation results on the maximum stress ( $\sigma_{max1}$ ), energy released ( $G_{c1}$ ) and Young's modulus (E) as a function of the cohesive strength by deforming the CNT-SiO<sub>2</sub> nanocomposite. (b1) The second peak simulation results on the maximum stress ( $\sigma_{max2}$ ) and energy released ( $G_{c2}$ ) as a function of the cohesive strength by deforming the CNT-SiO<sub>2</sub> nanocomposite.



Figure 4.8: (a2) The first peak simulation results on the maximum stress  $(\sigma_{\max 1})$ , energy released  $(G_{c1})$  and Young's modulus (E) by deforming the silica structure with a hole. (b2) The second peak simulation results on the maximum stress  $(\sigma_{\max 2})$  and energy released  $(G_{c2})$  by deforming the silica structure with a hole.



Relative Change (CNT-Silica Composite, Silica Structure with a Hole<sub>reference</sub>)

Figure 4.9: (a3) The relative difference between the mechanical properties of the  $CNT-SiO_2$  nanocomposite and the silica structure with a hole (reference) for the first peak results. (b3) The relative difference between the mechanical properties of the  $CNT-SiO_2$  nanocomposite and the silica structure with a hole (reference) for the second peak results.



**Figure 4.10:** (a1-a4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite by applying 0.05ev cohesive strength. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite by applying 0.1ev cohesive strength.



Figure 4.11: (a1)-(a2) The first peak simulation results on the maximum stress  $(\sigma_{\max 1})$  and energy released  $(G_{c1})$  as a function of the cohesive strength by deforming the CNT-SiO<sub>2</sub> nanocomposite. (b1)-(b2) The second peak simulation results on the maximum stress  $(\sigma_{\max 2})$  and energy released  $(G_{c2})$  as a function of the cohesive strength by deforming the CNT-SiO<sub>2</sub> nanocomposite.



Figure 4.12: (a) The first peak simulation results on the maximum stress  $(\sigma_{\max 1})$ and energy released  $(G_{c1})$  by deforming the silica structure with a hole. (b) The second peak simulation results on the maximum stress  $(\sigma_{\max 2})$  and energy released  $(G_{c2})$  by deforming the silica structure with a hole.



Figure 4.13: (a1) The relative difference of  $\sigma_{\text{max1}}$  between the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference). (a2) The relative difference of  $G_{c1}$  between the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference). (b1) The relative difference of  $\sigma_{\text{max2}}$  between the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference). (b2) The relative difference of  $G_{c2}$  between the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference). (b2) The relative difference of  $G_{c2}$  between the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference). (b2) The relative difference of  $G_{c2}$  between the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference).



**Figure 4.14:** (a1-a4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite by applying 0.005ev cohesive strength. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite by applying 0.05ev cohesive strength.



Figure 4.15: (a1-a4) During the uni-axial tension test, a sequence of snapshots of stress  $(\sigma_{yy})$  distribution in CNT-SiO<sub>2</sub> nanocomposite by applying 0.1ev cohesive strength. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress  $(\sigma_{yy})$  distribution in CNT-SiO<sub>2</sub> nanocomposite by applying 0.15ev cohesive strength.



Figure 4.16: The CNT-SiO<sub>2</sub> nanocomposite with different nanotube radius (area fraction) set up (a1: 0.5%, a2: 1.5%, a3: 2.5%, a4: 3.5%, a5: 7%, a6: 8%, a7: 9%, a8: 10%).



Figure 4.17: (a1) The first peak simulation results on the maximum stress  $(\sigma_{\max 1})$ , energy released  $(G_{c1})$  and Young's modulus (E) as a function of the area fraction of the nanotube in domain by deforming the CNT-SiO<sub>2</sub> nanocomposite. (b1) The second peak simulation results on the maximum stress  $(\sigma_{\max 2})$  and energy released  $(G_{c2})$  as a function of the area fraction of the nanotube in domain by deforming the CNT-SiO<sub>2</sub> nanocomposite.



Figure 4.18: (a2) The first peak simulation results on the maximum stress  $(\sigma_{\max 1})$ , energy released  $(G_{c1})$  and Young's modulus (E) as a function of the area fraction of the hole in domain by deforming the silica structure with a hole. (b2) The second peak simulation results on the maximum stress  $(\sigma_{\max 2})$  and energy released  $(G_{c2})$  as a function of the area fraction of the hole in domain by deforming the silica structure with a hole.



Relative Change (CNT-Silica Composite, Silica Structure with a Hole<sub>reference</sub>)

Figure 4.19: (a3) The relative difference between the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference) for the first peak results. (b3) The relative difference between the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposite and the silica structure with a hole (reference) for the second peak results.



Figure 4.20: (a1-a4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite and the area fraction of the nanotube in domain is 3.0%. (b1-b4) During the uni-axial tension test, a sequence of snapshots of stress ( $\sigma_{yy}$ ) distribution in CNT-SiO<sub>2</sub> nanocomposite and the area fraction of the nanotube in domain is 3.5%.

#### Chapter 5

# THE RADIUS EFFECTS ON SILICA STRUCTURE WITH A HOLE IN CONTINUUM SCALE

In this section, we will study how the radius of the hole effects the mechanical properties of the silica structure, then we will compare the continuum results to the sub-micron results (see section 4.6) to understand how to design the silica structure in multi-scale modeling.

### 5.1 The Mesh Convergence Study

In finite element modeling, a finer mesh study results in a more accurate solution. However, as the mesh becomes finer, the computation cost also increases. Therefore, a mesh size that can balance between the result accuracy and computational cost is desired. To achieve this balance, a mesh convergence study is performed. There are 3 steps to the mesh convergence study. First, create a mesh using the fewest and reasonable number of elements to analysis the result. Second, recreate the mesh by using finer elements, then analysis the results and compare the results to the previous one. Third, keep increasing the mesh number until the analysis results converge satisfactorily. In this section, the mesh convergence study will be performed by using the silica structure with a hole as shown in the Fig.5.1.



Figure 5.1: The top view of the silica structure with  $L_x = 1028$ Å,  $L_y = 849$ Å, d = 103.2Å,  $l_c = 100$ Å and  $l_n = 100$ Å.

To compare with the molecular dynamics simulations, the  $L_x$ ,  $L_y$ ,  $l_n$  and  $l_c$ for the silica structure with a hole shown in the Fig.5.1 are identical compare to the molecular structures we studied in the section 4.6 (see Fig.4.16) and in this case, the area fraction of the hole is 1.0% (d = 103.2Å). Then from coarse to fine, the mesh is created as shown in the Fig.5.2 and table 5.1.

After that, the uni-axial tension tests are applied to those systems, the maximum stress, energy release and Young's modulus are calculated for each mesh size

Mesh Size	Number of Elements on domain
6	256
4	540
2	2143
1.5	3606
1.0	7928
0.8	12777

Table 5.1: The number of elements on domain and its corresponding mesh size.





set up. The results are shown in the Fig.5.3.



**Figure 5.3:** Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of number of elements on domain.
From the Fig.5.3, we can see that the maximum stress (fracture strength or  $\sigma_{\text{max}}$ ), energy released (G) and Young's modulus (E) are convergence when the element number increases, this is because when a mesh size is small enough in a model, the results of an analysis will not be affected by keeping decreasing the mesh size. Therefore, the mesh size of 1.0 is chosen to balance between the result accuracy and computational cost.

# 5.2 The Fracture Mechanism of the Silica Structure with a Hole in Continuum Scale

In order to model the failure of the silica structure under the uni-axial tension test in continuum scale, the cohesive zone model is applied to the system. In a cohesive zone model, we assume that there is a narrow band with infinitesimal thickness at the head of the crack tip called cohesive zone which is shown in the Fig.5.4. The upper and lower cohesive surfaces are acted by the cohesive traction following the cohesive constitutive law which is the relationship between the cohesive traction and the separation distance between the upper and lower cohesive surfaces [51]. When crack is nucleated, the separation distance of the cohesive surfaces increases as the cohesive traction increases. Until the cohesive traction reaches to its criteria (the maximum value defined by user) and then suddenly drop to 0, the crack starts to grow which results in complete separation of the material.

In our case, the criteria is based on the maximum principal stress, the crack starts to grow when the maximum principal stress reaches a critical value (f = 1) as



Figure 5.4: The cohesive zone ahead of a crack.

shown in equation 5.1:

$$f = \frac{\sigma_n}{\sigma_{max}^0} \tag{5.1}$$

For example, we set the value of  $\sigma_{max}^0$  is equal to 49GPa which is comparable with the maximum stress of silica by using Tersoff potential. Then the uni-axial tension test is applied to a silica structure, the structure is shown in the Fig.5.7 a4. During the uni-axial tension test, the silica structure and its maximum principal stress distribution ( $\sigma_n$ ) are shown in the Fig.5.5.

From the Fig.5.5(b1) and (c1), we can see that right before the crack propagation, the  $\sigma_n$  at the crack tip is equal to 48.89GPa which is close but still smaller than the  $\sigma_{max}^0$  (49GPa). Therefore, the crack is nucleation as shown in the Fig.5.5(a1). Then, After one timestep which is shown in the Fig.5.5(b2) and (c2), the  $\sigma_n$  at the crack tip increases from 48.89GPa to 49.19GPa which is larger than the  $\sigma_{max}^0$ 



Figure 5.5: (a1)(b1) The maximum principal stress in y direction  $(\sigma_n)$  distributes in the silica structure right before the crack propagation and the magnifying image of the crack. (a2)(b2) The maximum principal stress in y direction  $(\sigma_n)$  distributes in the silica structure right after the crack propagation and the magnifying image of the crack.

(49GPa). From the Fig.5.5(a2), we can see that, the crack starts to propagate since the maximum principal stress has already met its critical value which is  $f = \frac{\sigma_n}{\sigma_{max}^0} > 1$ .

Finally, the stress vs strain curve of the silica structure with a hole (r = 102.8



Å) under uni-axial tension test is shown in the Fig.5.6.

Figure 5.6: The stress vs strain curve of the silica structure with a hole (R = 102.8 Å) under uni-axial tension test in the continuum scale. And sequence of snapshots of maximum principal stress  $(\sigma_n)$  distribution in the silica structure (a-f).

From the Fig5.6, we can see that, the stress vs strain curve and the crack propagation of the silica structure in continuum scale is comparable with the molecular dynamics simulations (see Fig.4.4 and Fig.4.6). From the Fig.5.6, we can see that before the deformation, the structure is free of stress which is shown in the Fig.5.6 (a). Then during the deformation, the stress starts to nucleate at the crack tip and the local stress around the crack tip is gradually increased until the maximum principal stress ( $\sigma_n$ ) at the crack tip is higher than its critical value ( $\sigma_{max}^0 = 49$ GPa), then the crack starts to grow as shown in the Fig.5.6 (b). Since the presenting of the hole stops the crack growing, the stress starts to nuclear at the right edge of the hole as shown in the Fig.5.6 (c). When the maximum principal stress ( $\sigma_n$ ) at the right edge of the hole is higher than its critical value ( $\sigma_{max}^0 = 49$ GPa), the crack starts to propagate at the right edge as shown in the Fig.5.6 (e). Finally the structure is totally failed and the stress is released as shown in the Fig.5.6 (f).

#### 5.3 The Radius Effects

In this section, we will study how the radius of the hole effects the mechanical properties of the silica structure. The structure is created by inserting a hole into the silica matrix with different radius (see table 5.2 and Fig.5.7). From the Fig.5.7, we can see that the values of  $L_x$ ,  $L_y$ ,  $L_z$ ,  $l_n$  and  $l_c$  are from the structure we studied in section 5.1 (see Fig.5.1) and the only difference is the radius of the hole.

Area Fraction of the Hole in Domain (%)	Radius of the Hole (Å)
1.0	51.6
2.0	72.7
3.0	88.9
4.0	102.8
5.0	115.1
6.0	125.9
7.0	135.9

**Table 5.2:** The area fraction of the hole in domain and its corresponding radius.

Then, the uni-axial tension tests (see section 2.2) are applied to the system. After that, the maximum stress, energy release and Young's modulus are calculated for each radius set up. The results are shown in the Fig.5.8.

From the Fig.5.8(a), we can not see obvious relationship between the fracture strength and the radius of hole. However, in molecular dynamics simulations, we can clearly see that when the radius of hole decreases, the fracture strength decreases (see section 4.6). Why did continuum simulations give a different result compare to molecular dynamics simulations? The answer is that the cohesive zone model dose not represent any material physically, but describes the cohesive traction before the separation of material elements. Since in continuum scale, the stress at the crack tip is infinite in mathematics, and which is not the case in real life. Therefore, the cohesive zone model dose not involve stress singularity at the crack tip, and material failure is controlled by other quantities such as stress and strain[51]. Therefore, we can not describe the stress field accurately at the crack tip in continuum scale. However, in molecular dynamics simulations, since the physical movements of atoms are the only consideration and which is totally independent of the material geometry. Therefore, it can describe the stress field at the crack tip more accurate than classical fracture mechanics. That is why in molecular dynamics simulations, we can see the relationship between the fracture strength and the radius of hole, but in continuum scale, we can not.

From the Fig.5.8(b), we can see that when the radius of the hole increases, the toughness also increases. This is because when the radius of the hole increases, the curvature at the hole edges decreases. When the stress starts to concentrate at the right edge of the hole, at the edge which has larger curvature, the stress is easier to concentrate, and at the edge which has smaller curvature, the stress is harder to concentrate. That is why when the radius of the hole increases, the toughness also increases. According to the power law, we can fit the MD data points to a curve to represent the relationship between the radius of the hole and the toughness  $(G_c)$ . The function of the fitted curve is shown below:

$$G_c(x) = -15.59 + 18.04 \times x^{-0.01778}$$
(5.2)

From the Fig.5.8(c), we can see that when the radius of the hole increases, the Young's Modulus linearly decreases which is highly comparable with molecular dynamics simulations (see section 4.6 and Fig.4.18). When radius of the hole increases, the material in the silica structure decreases. At same strain, less material in the structure means the amount of deforming energy observed by that structure decreases, and this leads to the decreasing of Young's Modulus. According to the power law, we can fit the MD data points to a curve to represent the relationship between the radius of the hole and the Young's Modulus (E). The function of the fitted curve is shown below:

$$E(x) = -140.8 + 87.56 \times x^{0.9598} \tag{5.3}$$



Figure 5.7: The silica structure with different hole radius (area fraction) set up (a1: 1%, a2: 2%, a3: 3%, a4: 4%, a5: 5%, a6: 6%, a7: 7%).



**Figure 5.8:** Simulation results on the maximum stress (fracture strength or  $\sigma_{\max}$ ), energy released (G) and Young's modulus (E) as a function of the hole radius.

### Chapter 6

### **CONCLUSIONS & FUTURE WORK**

The key contributions of this thesis are list below:

- 1. Amorphous Silica
  - (a) Presenting the structure and mechanical properties of amorphous silica in molecular dynamics simulations by using ReaxFF potential and the results are comparable with experience observations.
- 2. Carbon Nanotube
  - (a) The mechanical properties of carbon nanotube in axial direction is much stronger than lateral direction.
- 3. CNT-SiO<sub>2</sub> Nanocomposite
  - (a) Interfacial Strength Study
    - i. The results show that different interfacial strength can extraordinarily change the fracture strength and toughness. There is a corresponding and mathematical relationship between interfacial strength and strength-toughness of CNT-Silica nanocomposite. A relative increase in interfacial strength gives drop to a proportional relative increase in toughness and strength. When interfacial strength is high enough, keep increasing interfacial strength will not effect the toughness and strength any more. When interfacial strength is low enough, the toughness and strength of CNT-Silica nanocomposite will be same compare to the silica-hole structure with the same radius.

- (b) Nanotube Radius Study
  - i. The results show that different nanotube radius can extraordinarily change the fracture strength, toughness and Young's modulus of CNT-Silica nanocomposite. There is a corresponding relationship between nanotube radius and strength of CNT-Silica nanocomposite, as well as radius and toughness, radius and Young's modulus. When nanotube radius increases, the fracture strength, toughness and Young's modulus linearly decrease.
- (a) The Radius Effects on Silica Structure with a Hole in Continuum Scale
  - i. The results show that different hole radius can extraordinarily change the toughness and Young's modulus of the silica structure. There is a corresponding and mathematical relationship between hole radius and Young's modulus, as well as hole radius and toughness. A relative increase in hole radius gives drop to a proportional relative increase in toughness. When hole radius is high enough, keep increasing hole radius will not effect the toughness any more. And when hole radius increases, the Young's modulus linearly decreases.

For the future work, more complicated geometrically identifiable nanotube configurations will be generated to study the toughness-strength correlation of the nanocomposite. Here are few examples. From the Fig.6.1(a), we can see that, two nanotubes with different radius have been inserted into a silica matrix with a line arrangement and in the Fig.6.1(b), the two nanotubes have exchanged their positions. By deforming those 2 structures, we can find out whether or not those two identical but asymmetric configurations can have equal fracture strength and stiffness but dissimilar toughness.

More complicated geometrically identifiable nanotube configurations are shown in the Fig.6.2. In this case, we want to know that whether or not the positions and the



Figure 6.1: The CNT-SiO<sub>2</sub> nanocomposites with line nanotube configurations.

number of carbon nanotubes can change the fracture strength, stiffness and toughness. How the nanotube configuration rotation change their macroscopic toughness and how the crack propagation in those cases.

Finally, by using those results we can predict the architecture that optimizes the macroscopic toughness, strength and stiffness.



Figure 6.2: (a) The CNT-SiO<sub>2</sub> nanocomposite with triangle nanotube configuration. (b) The CNT-SiO<sub>2</sub> nanocomposite with square nanotube configuration. (c) The CNT-SiO<sub>2</sub> nanocomposite with pentagon nanotube configuration. (d) The CNT-SiO<sub>2</sub> nanocomposite with hexagon nanotube configuration.

#### REFERENCES

- [1] Geology, "Granite: What is granite? what is granite used for?." http: //geology.com/rocks/granite.shtml, 2017.
- [2] Pinterest, "Granites with different colors." https://www.pinterest.com/pin/ 310959549241639122/, 2017.
- [3] Boeing, "Introducing the 777x." http://www.boeing.com/commercial/777x/ /, 2017.
- [4] H. Caliendo, "Battle of the composite wings." http://www.compositesworld. com/blog/post/battle-of-the-composite-wings-, 2015.
- [5] G. Norris and J. Anselmo, "777x production investments bolster boeing." http://aviationweek.com/commercial-aviation/ 777x-production-investments-bolster-boeing, 2016.
- [6] C. Buzea, I. I. Pacheco, and K. Robbie, "Nanomaterials and nanoparticles: Sources and toxicity," *Biointerphases*, vol. 2, no. 4, pp. MR17–MR71, 2007.
- [7] P. Nemes-Incze, Z. Osváth, K. Kamarás, and L. Biró, "Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy," *Carbon*, vol. 46, no. 11, pp. 1435–1442, 2008.
- [8] M.-S. Wang, D. Golberg, and Y. Bando, "Tensile tests on individual singlewalled carbon nanotubes: Linking nanotube strength with its defects," *Advanced Materials*, vol. 22, no. 36, pp. 4071–4075, 2010.
- [9] A. Krishnan, E. Dujardin, T. Ebbesen, P. Yianilos, and M. Treacy, "Youngs modulus of single-walled nanotubes," *Physical Review B*, vol. 58, no. 20, p. 14013, 1998.
- [10] Nanoscience, "Cnt technology overview." http://www.nanoscience.com/ applications/education/overview/cnt-technology-overview/, 2017.

- [11] G. Lalwani, A. M. Henslee, B. Farshid, L. Lin, F. K. Kasper, Y.-X. Qin, A. G. Mikos, and B. Sitharaman, "Two-dimensional nanostructurereinforced biodegradable polymeric nanocomposites for bone tissue engineering," *Biomacromolecules*, vol. 14, no. 3, pp. 900–909, 2013.
- [12] Britannica, "Silica." https://www.britannica.com/science/silica, 2017.
- [13] M. N. Rahaman, D. E. Day, B. S. Bal, Q. Fu, S. B. Jung, L. F. Bonewald, and A. P. Tomsia, "Bioactive glass in tissue engineering," *Acta biomaterialia*, vol. 7, no. 6, pp. 2355–2373, 2011.
- [14] J. Velez, "Ceramic biomaterials." http://www.openwetware.org/wiki/ Ceramic\_Biomaterials%2C\_by\_Jon\_Velez, 2014.
- [15] J. Nye, "Terror at 1,353ft: They said it was unbreakable but this was the horrifying moment chicago tower block's 103rd floor glass viewing platform cracked under tourists' feet." http://www.dailymail.co.uk/news/article-2642967/ They-said-unbreakable-Tourists-shock-lives-glass-floor-Willis-Towers-Ledge-crack html, 2014.
- [16] B. Larson, "Ndt education resource center developed by the collaboration for ndt education," *Center for Nondestructive Evaluation, Iowa State University, Ames, Iowa*, vol. 50011, 2001.
- [17] AZoM, "Silica silicon dioxide (sio2)." http://www.azom.com/article.aspx? ArticleID=1114, 2001.
- [18] H.-S. P. W. MAX SHULAKER and S. MITRA, "How well put a carbon nanotube computer in your hand." http://spectrum.ieee.org/semiconductors/ devices/how-well-put-a-carbon-nanotube-computer-in-your-hand, 2016.
- [19] D. W. Brenner, "The art and science of an analytic potential," physica status solidi(b), vol. 217, no. 1, pp. 23–40, 2000.
- [20] M. Z. Hossain, "Chemistry at the graphene-sio2 interface," Applied Physics Letters, vol. 95, no. 14, p. 143125, 2009.
- [21] J. Tersoff, "New empirical approach for the structure and energy of covalent systems," *Physical Review B*, vol. 37, no. 12, p. 6991, 1988.

- [22] E. Lee, K.-R. Lee, M. Baskes, and B.-J. Lee, "A modified embedded-atom method interatomic potential for ionic systems: 2 nnmeam+ qeq," *Physical Review B*, vol. 93, no. 14, p. 144110, 2016.
- [23] G. Abell, "Empirical chemical pseudopotential theory of molecular and metallic bonding," *Physical Review B*, vol. 31, no. 10, p. 6184, 1985.
- [24] A. C. Van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard, "Reaxff: a reactive force field for hydrocarbons," *The Journal of Physical Chemistry A*, vol. 105, no. 41, pp. 9396–9409, 2001.
- [25] T. P. Senftle, S. Hong, M. M. Islam, S. B. Kylasa, Y. Zheng, Y. K. Shin, C. Junkermeier, R. Engel-Herbert, M. J. Janik, H. M. Aktulga, *et al.*, "The reaxff reactive force-field: development, applications and future directions," *npj Computational Materials*, vol. 2, p. 15011, 2016.
- [26] S. J. Stuart, A. B. Tutein, and J. A. Harrison, "A reactive potential for hydrocarbons with intermolecular interactions," *The Journal of chemical physics*, vol. 112, no. 14, pp. 6472–6486, 2000.
- [27] S. Plimpton, P. Crozier, and A. Thompson, "Lammps-large-scale atomic/molecular massively parallel simulator," *Sandia National Laboratories*, vol. 18, 2007.
- [28] N. Liao, W. Xue, H. Zhou, and M. Zhang, "Investigation on high temperature fracture properties of amorphous silicon dioxide by large-scale atomistic simulations," *Journal of Materials Science: Materials in Electronics*, vol. 24, no. 5, pp. 1575–1579, 2013.
- [29] F. Yuan and L. Huang, "Molecular dynamics simulation of amorphous silica under uniaxial tension: From bulk to nanowire," *Journal of Non-Crystalline Solids*, vol. 358, no. 24, pp. 3481–3487, 2012.
- [30] M. J. Buehler, A. C. van Duin, and W. A. Goddard III, "Multiparadigm modeling of dynamical crack propagation in silicon using a reactive force field," *Physical review letters*, vol. 96, no. 9, p. 095505, 2006.
- [31] S. C. Chowdhury, B. Z. G. Haque, and J. W. Gillespie, "Molecular dynamics simulations of the structure and mechanical properties of silica glass using reaxff," *Journal of Materials Science*, vol. 51, no. 22, pp. 10139–10159, 2016.

- [32] Y. Yu, B. Wang, M. Wang, G. Sant, and M. Bauchy, "Revisiting silica with reaxff: Towards improved predictions of glass structure and properties via reactive molecular dynamics," *Journal of Non-Crystalline Solids*, vol. 443, pp. 148– 154, 2016.
- [33] R. Laughlin, J. Joannopoulos, and D. Chadi, "Bulk electronic structure of si o 2," *Physical Review B*, vol. 20, no. 12, p. 5228, 1979.
- [34] T. Yi, L. Li, and C.-J. Kim, "Microscale material testing of single crystalline silicon: process effects on surface morphology and tensile strength," *Sensors and Actuators A: Physical*, vol. 83, no. 1, pp. 172–178, 2000.
- [35] D. L. Griscom, "Self-trapped holes in amorphous silicon dioxide," *Physical Review B*, vol. 40, no. 6, p. 4224, 1989.
- [36] S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," *Journal of computational physics*, vol. 117, no. 1, pp. 1–19, 1995.
- [37] E. R. Cruz-Chu, A. Aksimentiev, and K. Schulten, "Water-silica force field for simulating nanodevices," *The Journal of Physical Chemistry B*, vol. 110, no. 43, pp. 21497–21508, 2006.
- [38] J. Holt, "Uniaxial tension testing.," Materials Park, OH: ASM International, 2000., pp. 124–142, 2000.
- [39] J. Wortman and R. Evans, "Young's modulus, shear modulus, and poisson's ratio in silicon and germanium," *Journal of applied physics*, vol. 36, no. 1, pp. 153– 156, 1965.
- [40] M. Mellor and D. M. Cole, "Deformation and failure of ice under constant stress or constant strain-rate," *Cold Regions Science and Technology*, vol. 5, no. 3, pp. 201–219, 1982.
- [41] H. Zhao, K. Min, and N. Aluru, "Size and chirality dependent elastic properties of graphene nanoribbons under uniaxial tension," *Nano letters*, vol. 9, no. 8, pp. 3012–3015, 2009.
- [42] M. Chen, S. Quek, Z. Sha, C. Chiu, Q. Pei, and Y. Zhang, "Effects of grain size, temperature and strain rate on the mechanical properties of polycrystalline graphene–a molecular dynamics study," *Carbon*, vol. 85, pp. 135–146, 2015.

- [43] J. Johnson, R. Weber, and M. Grimsditch, "Thermal and mechanical properties of rare earth aluminate and low-silica aluminosilicate optical glasses," *Journal* of non-crystalline solids, vol. 351, no. 8, pp. 650–655, 2005.
- [44] P. K. Gupta and C. R. Kurkjian, "Intrinsic failure and non-linear elastic behavior of glasses," *Journal of non-crystalline solids*, vol. 351, no. 27, pp. 2324–2328, 2005.
- [45] H. Scholze and S. Glass-Nature, "Properties," 1991.
- [46] K. Muralidharan, J. Simmons, P. Deymier, and K. Runge, "Molecular dynamics studies of brittle fracture in vitreous silica: Review and recent progress," *Journal* of non-crystalline solids, vol. 351, no. 18, pp. 1532–1542, 2005.
- [47] B. Yakobson, M. Campbell, C. Brabec, and J. Bernholc, "High strain rate fracture and c-chain unraveling in carbon nanotubes," *Computational Materials Science*, vol. 8, no. 4, pp. 341–348, 1997.
- [48] S. Deb Nath and S.-G. Kim, "Study of the nanomechanics of cnts under tension by molecular dynamics simulation using different potentials," *ISRN Condensed Matter Physics*, vol. 2014, 2014.
- [49] K. Liew, X. He, and C. Wong, "On the study of elastic and plastic properties of multi-walled carbon nanotubes under axial tension using molecular dynamics simulation," Acta Materialia, vol. 52, no. 9, pp. 2521–2527, 2004.
- [50] Wikipedia, "Carbon nanotube Wikipedia, the free encyclopedia," 2004. [Online; accessed 1-October-2005].
- [51] Z.-H. Jin and C. Sun, "A comparison of cohesive zone modeling and classical fracture mechanics based on near tip stress field," *International journal of solids* and structures, vol. 43, no. 5, pp. 1047–1060, 2006.

## Appendix A

## COHESIVE STRENGTH EFFECTS MECHANICAL PROPERTIES OF SILICA

Cohesive Strength (ev)	$\sigma_{\rm max1}$ (GPa)	$G_{c1} (\mathrm{J/m^3})$	E (GPa)
Silica	14.819	1.243	85.013
0.005	14.823	1.244	84.808
0.010	14.794	1.246	86.187
0.050	14.756	1.268	86.056
0.100	15.923	1.423	87.050
0.150	15.889	1.403	87.553
0.200	15.960	1.425	87.624
0.250	15.968	1.422	88.076
0.300	16.064	1.423	88.175
0.350	16.104	1.449	88.266

**Table A.1:** The mechanical properties of the silica structure with a hole (first peak) and the mechanical properties of the CNT-SiO<sub>2</sub> nanocomposites by applying different cohesive strength (first peak).