IMPROVEMENT OF THERMOELECTRIC PROPERTIES IN NANOSTRUCTURES WITH CONSTRICTIONS

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"All we have to decide is what to do with the time that is given us."

J.R.R. Tolkien

ABSTRACT

The results of a study into the development of novel Thermoelectric (TE) materials by engineering nanoscale constrictions are presented in this thesis. The aim of this investigation lies in the development of an enhanced TE material. To achieve this, the dependence of TE properties, specifically the TE figure of merit (ZT) on the material properties has been considered. The enhancement of the ZT was achieved by reducing the thermal conductivity (k) of the material. During this phase, the effects of different nanoscale modifications to the material structure on its electrical properties are contemplated to ensure that the TE ZT does not get vitiated.

Here, a novel nanostructure formed by the sintering of individual Silicon nanoparticles in a linear fashion has been used and is referred to as a Nanoparticle Chain (NPC) structure. The nanoparticle arrangement in an NPC structure causes nanoscale constrictions to be formed along the transport direction of the structure. This is seen to cause extremely low lattice k (reaching 0.614 W/mK) while preserving a considerable amount of crystallinity. The fabrication procedure of the NPC structure has also been considered through this study thereby ensuring that results can be translated to real-world applications using existing technologies. During the investigation, an interesting competing effect between two, phonon transport aspects has been observed to cause a nonmonotonic trend in the k of the structure, while a variation in the phonon density of states along the transport direction was identified to cause a k reduction to values lower than those attained with comparably sized nanowires.

Further variations of the structure are obtained by expanding the zero-dimensional constriction of NPC structures to a one-dimensional form referred to as Nanowire Chain (NWC) structures. Subsequently, the electrical properties of the structures in consideration are evaluated, and a three-order of magnitude enhancement in the TE ZT is observed in comparison to the bulk material. Thus, it is shown that nanoscale constrictions can be engineered to enhance the TE performance of materials.

Keywords: *Nanoparticles, Thermoelectric, Phonon transport, Electron transport, Ab-initio modelling, Constriction engineering*

PUBLICATIONS

Journal Articles

- P. Henadeera, N. Samaraweera, C. Ranasinghe, and A. Wijewardane, "Ultra-low thermal conductivity of nanoparticle chains: A nanoparticle based structure for thermoelectric applications," *J. Appl. Phys.*, vol. 130, no. 6, p. 064301, Aug. 2021.
- P. Henadeera, N. Samaraweera, C. Ranasinghe, and A. Wijewardane, "Surface and constriction engineering of nanoparticle based structures towards ultra-low thermal conductivity as thermoelectric materials," *Nanoscale and Microscale Thermophysical Engineering.*, Minor revisions pending.
- P. Henadeera, N. Samaraweera, C. Ranasinghe, and A. Wijewardane, "Notable thermoelectric performance of laterally arranged Si nanowires: Constriction engineering as a promising pathway." Submitted.

Conference Articles

- P. Henadeera, N. Samaraweera, C. Ranasinghe, and A. Wijewardane, "Ultra-low Thermal Conductivity Through Nano-Constriction Engineering," *13th Multidisciplinary International Student Workshop (MISW2022), Tokyo Institute of Technology*, p 43, 2022.

This thesis is dedicated to my wife and my parents.

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DECLARATION

I declare that this is my own work, and this thesis does not incorporate without acknowledgement any material previously published or submitted for a degree or diploma in any other university or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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PB Henadeera Date

The above candidate has carried out research for the doctoral dissertation under my supervision.

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NOMENCLATURE

Abbreviations

0D	Zero Dimensional
1D	One Dimensional
2D	Two Dimensional
BTE	Boltzmann Transport Equation
CBM	Conduction Band Minimum
COMPASS	Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies
CUDA	Compute Unified Device Architecture
DFT	Density Functional Theory
DMT	Derjaguin Müller Toporov
DoS	Phonon Density of States
DP	Deformation Potential
DZP	Double Zeta Polarized
EMD	Equilibrium Molecular Dynamics
GGA	Generalized Gradient Approximation
GK	Green Kubo
GPU	Graphics Processing Unit
GULP	General Utility Lattice Program
HCAF	Heat Current Autocorrelation Function
JKR	Johnson Kendall Roberts
LAMMPS	Large Scale Atomic/Molecular Massively Parallel Simulator
LD	Lattice Dynamics
LDA	Local Density Approximation
LJ	Lennard Jones
MCSN	Modulated Core Shell Nanowires
MD	Classical Molecular Dynamics
MEMS	Micro Electro-Mechanical Systems
MFP	Mean Free Path
NEMD	Non-Equilibrium Molecular Dynamics

NPB	Nanoparticle Packed Bed
NPC	Nano Particle Chain
NPM	Nano Particle Mesh
NWC	Nano Wire Chain
Ovito	Open Visualization Tool
PGEC	Phonon Glass/ Electron Crystal
PW	Plane-Wave
SA	Shell Alloyed
SA-1	Type-1 SA
SA-2	Type-2 SA
SED	Spectral Energy Density
SEM	Scanning Electron Microscopy
SW	Stillinger Weber
TE	Thermoelectric
TEG	Thermoelectric Generator
TEM	Transmission Electron Microscopy
VBM	Valance Band Maximum

Variables

Greek letters

σ	Electrical conductivity
η	Efficiency
Γ_i	Per Atom Stress Tensor
$\rho(\omega)$	Phonon density of states at omega frequency
ω	Frequency
ϕ	Potential energy
$\phi(x)$	Potential energy between two neighbors at a distance x from one another
$\phi\binom{ij}{ab}$	Energy of interaction between the i^{th} and j^{th} atoms in the a^{th} and b^{th} unit-cells

ω_0	Center of the Lorentzian function
Γ	Full width at half maximum of Lorentz function
τ	Relaxation time
$\psi_i(r)$	Wave function at location r
v_k	Velocity of electrons
τ_e	Relaxation time of electrons
$v_j(t)$	Velocity of the j^{th} atom at time t
n	Phonon normal mode
v	Phonon branch
ϕ_{Tot}	Total potential energy
$\lambda^* \binom{K\ i}{n\ \alpha}$	Conjugate of the eigenvector of the n^{th} mode at the wave vector K
$\boldsymbol{\lambda}_{i,n}$	Eigen vector of the i^{th} atom for the n^{th} normal mode
ε_i	Eigen energy of electrons

Roman letters

c	Speed of light
C	Elastic constant
d	Dimensionality of the system
D	Diffusion Coefficient
$\boldsymbol{D}$	The dynamical matrix
|Δ(DoS)|	Difference in Density of States
e	Charge of an electron
E	Electric field
E_1	The potential of deformation
E_{atom}	Total energy of an atom in equilibrium
E_{edge}	Energy of the band edge
E_{Lat}	Lattice energy
$E[n]$	Total energy of the system

E_{xc}	Exchange correlation energy
$\boldsymbol{F}$	Force constant matrix
$f_k(r,t)$	Distribution function
ħ	Reduced Planks constant
H	Magnetic field
$J_x(n)$	Heat Flux in the x Direction at Time $t = n$
k	Thermal conductivity
k_B	Boltzmann Constant
k_e	Electronic Thermal Conductivity
k_l	Lattice Thermal Conductivity
k_x	The thermal conductivity in x direction
K	Wave vector
$\Delta l/l_0$	Applied strain
L	Lorentz Number
m_e	Mass of electron
m_i	Mass of the i^{th} atom
N	Total Number of Atoms
N_{cell}	Total number of cells
P	Probability
PR	Participation Ratio
q	Heat Flux
$\boldsymbol{q}$	Heat Flux vector
$\dot{Q}$	Phonon normal mode coordinates
$\boldsymbol{r}$	Displaced position of atom
$\boldsymbol{r_0}$	Equilibrium position of atom
S	Seebeck coefficient
S_i	Per-atom stress tensor
t	Time
T	Absolute Temperature
T_0	Sampling time
T_c	Cold side temperature

T_h	Hot side temperature
$T[n]$	Kinetic energy of the system
$\boldsymbol{u}$	Small displacement
$\tilde{u}$	Amplitude of the phonon
u_a	displacement vector component of each atom in the a^{th} unit cell
$U_\alpha\binom{a}{i}, t)$	α^{th} component of the velocity of the i^{th} atom in the a^{th} unit cell at time t
V	Volume of the System
V_0	Unstrained volume
V_{eff}	Effective external potential
V_{inf}	Infinitesimal volume
$V_{int}[n]$	Electron-electron interaction energy of the system
ZT	Figure of Merit

LIST OF APPENDICES