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**NANYANG
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SINGAPORE

**LASER-INDUCED
IN-FIBER CAPILLARY INSTABILITY
AND MATERIAL ENGINEERING**

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2019

**LASER-INDUCED
IN-FIBER CAPILLARY INSTABILITY
AND MATERIAL ENGINEERING**

ZHANG JING

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

2019.JAN.10

Date

WEI Lei

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 3 is published as J. Zhang, K. Li, T. Zhang, P. J. Buenconsejo, M. Chen, Z. Wang, M. Zhang, Z. Wang, and L. Wei, Laser induced in-fiber fluid dynamical instabilities for precise and scalable fabrication of spherical particles, *Advanced Functional Materials* 27, 1703245 (2017).

The contributions of the co-authors are as follows:

- Prof. WEI provided the initial project direction and edited the manuscript drafts.
- I finished the preform preparation, fiber fabrication, experiment system design, experiment setup construction, in-fiber particles fabrication, theory development, measurement of the Q value of silicon whispering gallery mode resonator, measurement of sphere size distribution, sample preparation for characterizations and paper writing.
- Dr. Kaiwei Li finished the preform preparation, fiber fabrication, measurement of the Q value of silicon whispering gallery mode resonator.
- Dr. Ting Zhang finished the preform preparation.
- Dr. P. J. Beunconseio assisted in achieving XRD characterization.
- M. Chen helped to test the surface roughness.
- Zhe Wang and Zhixun Wang assisted in polymer-based fiber fabrication.
- Mengying Zhang assisted in the experiment design of whispering gallery mode resonator.

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The contributions of the co-authors are as follows:

- Prof. WEI provided the initial project direction and edited the manuscript drafts.

- I finished the preform preparation, fiber fabrication, experiment system design, experiment setup construction, single crystal fiber fabrication, sample preparation for characterizations and paper writing.
- Dr. Ting Zhang, who contributed equally to this work, finished the preform preparation, SnSe fiber fabrication, measurement of ZT values and thermoelectric properties and paper writing.
- Prof. Haisheng Chen, Prof. Hang Zhang and Dr. Zhe Chen assisted in the measurement of thermoelectric properties.
- Zhixun Wang and Xingming Huang assisted in achieving XRD characterization, TEM and EBSD analysis.
- Prof. Zhifeng Ren and Dr. Shuo Chen and provides the high-temperature TEM characterization.
- Prof. Zhiting Tian and Dr. Li Chen achieved the simulation and calculation of ZT value for single crystal SnSe.
- Dr. Kaiwei Li and Zhe Wang assisted in fiber fabrication

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Table of Contents

Statement of Originality	I
Supervisor Declaration Statement.....	II
Authorship Attribution Statement	III
Acknowledgments	V
Table of Contents	VII
Summary	XI
List of Abbreviations	XIII
List of Figures.....	XV
Chapter 1 Introduction.....	1
1.1 Background and Motivation	1
1.2 Objectives	4
1.3 Major Contributions.....	4
1.4 Organization of the Thesis	6
Chapter 2 Literature Review	8
2.1 Introduction.....	8
2.2 Multimaterial Fibers.....	9
2.2.1 Preform Fabrication and The Preform-to-Fiber Thermal Drawing Processing	9
2.2.2 Materials Collocation and Selection	13
2.3 Multifunctional Fibers	16
2.3.1 Photonics Bandgap Fibers.....	17
2.3.2 Optoelectrical fibers	20
2.3.3 Energy Harvesting fibers	21

2.3.4 In-fiber Chemical Synthesis	25
2.3.5 Highly-Integrated Fiber-based Devices.....	28
2.4 In-fiber Micro and Nanoscale Structures Fabrication	31
2.4.1 In-fiber Micro- and Nanowires Fabrication	32
2.4.2 In-fiber Micro- and Nano-Spherical Particles Fabrication Based on Capillary Instability.....	35
2.5 In-fiber Materials Engineering	42
2.5.1 Laser Induced Recrystallization for Single Crystal Fiber Fabrication	42
2.5.2 Extreme Electronic Bandgap Modification in Multimaterial Fibers	43
2.6 Summary of Chapter 2	44
Chapter 3 In-fiber Particles Fabrication Based on Capillary Instability	46
3.1 Introduction	46
3.2 In-fiber Capillary Instability.....	47
3.2.1 Introduction to Capillary Instability	47
3.2.2 Thermal Treatment Induced In-Fiber Capillary Instability	49
3.3 Laser Induced In-fiber Capillary Instability	51
3.3.1 Background Information	51
3.3.2 Fiber Fabrication	52
3.3.3 Precisely Controlled Microscale Particles Fabrication	53
3.3.4 Spheres Fabrication down to Nanometer Scale.....	59
3.4 Characterization and Size Distribution of Generated Spheres	61
3.5 Application of The Silicon Spheres Generated from The Laser-Induced In-Fiber Capillary Instability	64
3.6 Summary of Chapter 3	66
Chapter 4 In-Fiber Material Engineering Based on Laser Recrystallization	67
4.1 Introduction	67

4.2 Functional Fiber Fabrication	68
4.3 Laser Recrystallization.....	71
4.3.1 Laser Thermal Treatment.....	71
4.3.2 Single Crystal Formation	73
4.3.3 Single Crystal Structure Characterization Based on Electron and X-ray Analysis.....	74
4.4 Thermoelectric Properties of The Generated Single Crystal SnSe Fiber	82
4.5 Application of The Generated Single Crystal SnSe Fiber	88
4.6 Summary of Chapter 4	89
Chapter 5 Fundamentals of Laser Thermal Treatment for In-Fiber Fabrication and Material Engineering	91
5.1 Introduction.....	91
5.2 CO ₂ Laser Heating Induced In-Fiber Phenomena and Their Applications.....	94
5.2.1 In-Fiber Built-In Stress	95
5.2.2 CO ₂ laser Induced In-Fiber Material Recrystallization	99
5.2.3 In-fiber Capillary Instability	103
5.2.4 In-fiber Laser Trapping and Movements of Generated In-Fiber Particles	109
5.3 Summary of Chapter 5	111
Chapter 6 Summary and Outlook	113
6.1 Outlook and Future Work	113
6.1.1 In-fiber Gradient-Index Micron Lens Fabrication Based-On the Precisely Controlled Built-In Stress	113
6.1.2 In-fiber PN Junction Particle Pairs with More Complex Structure and In- Fiber Integrated Devices	113
6.2 Summary and discussion.....	114

Appendix	116
Publications.....	117
Bibliography.....	119

Summary

The emerging of multimaterial fibers has been found with widespread applications in various areas. Towards the concept, preform-to-fiber thermal drawing method has been well-established which allows the fabrications of glass or polymer-based fibers with multifunctional internal structures. Besides, a wide range of materials, such as semiconductor, metal, doped-glass and functional polymer, have been drawn into fiber successfully by this method thereby researchers achieve photonics bandgap fiber, optoelectrical fiber, energy harvesting fiber, in-fiber chemical synthesis, etc. However, typical multimaterial fibers are fixed in an axially-invariant core/cladding structure after the drawing process. To increase the number of functional units in one multifunctional fiber, fabricating more complex structures in both fiber cross-section axial and fiber length axial is needed, in other words, ways to achieve micro/nano structures in-fiber are strongly needed. In addition, multifunctional fibers request more advanced materials with preferable properties, such as extremely low-loss optical materials and high-efficiency energy-harvesting crystal materials. But methods to modify the material properties of as-drawn fibers have not been well established, which limits multifunctional fibers to benefit from today's material sciences or to be used in wider areas.

Both in-fiber fabrication and materials engineering request innovations in multimaterial multifunctional fiber's development. In this thesis, we develop a new thermal treatment system based on a CO₂ laser as the heat source. The laser features (1) precisely controlled and stable heating profile; (2) gradient heat distribution; (3) adjustable heating temperature to fit various functional materials; (4) limited heating area. Utilizing the system, we can produce uniformly-sized and globally ordered in-fiber micro/nano-structures and to achieve direct material properties modifications inside the as-drawn fibers. Moreover, the precisely controlled laser heating process enables plenty of interesting in-fiber phenomena such as built-in stress, Plateau-Rayleigh capillary instability, laser-induced recrystallization and laser trapping of in-fiber objects accordingly at the heterogeneous interfaces along the entire length.

Once occurred on melted fiber materials during the laser heating process, surface-tension-driven capillary instability causes the initially continuous core to break up into a periodic particles array with uniform sizes. This capillary instability provides the possibility for the fabrication of in-fiber micro- and nanoscale spherical particles and structures, which is comprehensively studied in this thesis. We demonstrate that the size-controllable fabrications of micro to nanoscale spherical particles could be applied onto a wide range of functional materials (metal, doped glass, semiconductor, and functional polymer) with different melting temperatures from 400 to 2400 K. Optical properties of the fabricated spherical particles are also characterized, showing that an ordered array of silicon-based whispering gallery mode resonators with high Q factor can be achieved following our method.

Furthermore, by tuning the laser heating process through the controlling of multiple fabrication parameters, we gain the ability to engineer the properties of in-fiber materials. Indeed, we develop a recrystallization process to directly modify the in-fiber functional material. The CO₂ laser selectively heats a limited zone of the fiber and scans through the fiber to recrystallize the core by precisely controlling the cooling rate and heating temperature. Eventually, we realize a stable laser-induced recrystallization method and achieve a pressure-induced structural transition of single crystalline Tin Selenide (SnSe) core fiber in $Fm\bar{3}m$ cubic rock-salt phase with outstanding thermoelectric performance.

Next, more laser induced in-fiber phenomena that could be utilized for in-fiber fabrication and materials engineering are discussed. The laser-based system developed by us has adjustable parameters including laser heating power, spot size, and fiber feed-in velocity to control the in-fiber heating temperature and the cooling rate. This laser heating process can induce built-in stress, laser recrystallization, in-fiber capillary instability, and laser trapping into the multimaterial fiber. We also study the laser induced heating process in fundamental by theoretical modeling and software simulations. The study offers us the capability of fabricating electric bandgap adjustable devices, high-quality single crystal fiber devices, uniform or asymmetry shaped micro/nano-particles as well as spheres PN molecules.

List of Abbreviations

AFM	Atomic Force Microscope
COP	Cyclic Olefin Polymer
CPC	Conductive Polycarbonate
CPE	Conductive Polyethylene
CW	Continuous Wave
DFT	Density-Functional Theory
EBSD	Electron Back Scatter Diffraction
EDS	Energy-Dispersive X-Ray Spectroscopy
FIB	Focused Ion Beam
GGA	Generalized Gradient Approximation
HF	Hydrofluoric Acid
HPCVD	High-Pressure Chemical Vapor Deposition
LO-TO	Longitudinal and Transverse Optical
LTEC	Linear Thermal Expansion Coefficient
PBE	Perdew-Burke-Ernzerhof
PBG	Photonics Bandgap
PC	Polycarbonate
PE	Polyethylene

PR	Plateau-Rayleigh
PSU	Polysulfone
PVDF	Poly(Vinylidene Fluoride)
Q Factor	Quality Factor
QDs	Quantum Dots
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscope
TDTR	Time-Domain Thermoreflectance
TE	Thermoelectric
TEM	Transmission Electron Microscope
TENG	Triboelectric Nanogenerator
WGM	Whispering Gallery Mode
XRD	X-Ray Diffractometer
ZT value	A Dimensionless Thermoelectric Figure of Merit
T_B	Boiling Temperature
T_m	Melting Temperature
v_c	Critical Velocity of Single Crystal Growth

List of Figures

Figure 2-1: Rod-in-Tube approach for preform fabrication of thermal drawing processing.....	10
Figure 2-2: Multicore preform fabrication based on a rod-in-tube approach for thermal drawing processing.....	10
Figure 2-3: Thin-film rolling approach for thermal drawing processing perform fabrication.....	11
Figure 2-4: Sandwich consolidation approach for thermal drawing processing perform fabrication.	12
Figure 2-5: Schematic of the multimaterial fiber fabrication based on the thermal drawing process.....	13
Figure 2-6: Dynamic viscosity, melting/glass transition temperature and the linear thermal expansion coefficient of selected materials.....	15
Figure 2-7: SEM images of PBG fibers cross-section for high-power laser transmission.....	18
Figure 2-8: Azimuthally polarized radial lasing fibers.....	19
Figure 2-9: Liquid-crystal directional emission control of an azimuthally polarized radial lasing fiber.	19
Figure 2-10: Chemiluminescent vapor sensing based on PBG fibers.	20
Figure 2-11: Optoelectrical integrated fiber devices.	20
Figure 2-12: Schematics and operating principle of piezoelectric fibers.....	22
Figure 2-13: Schematics and operating principle of thermoelectric fibers.	23
Figure 2-14: Schematics and operating principle of triboelectric fibers.	25
Figure 2-15: Crystalline silicon core fiber fabrication and forming mechanism.	26
Figure 2-16: ZnSe core fiber in situ fabrication based on in-fiber synthesis.....	27

Figure 2-17: <i>In situ</i> alignment of carbon nanofiber fabricated by a thermal drawing process.	27
Figure 2-18: Multimaterial integrated fiber-devices.....	30
Figure 2-19: Breakup of multilayers into nanoscale structure based on fluid instability during multimaterial fiber thermal drawing process.	32
Figure 2-20: Fabrication of in-fiber nanoscale structures based on the thermal drawing process.	34
Figure 2-21: Characterization of fabricated nanowires.....	35
Figure 2-22: Size-controllable spherical particle generation based on in-fiber capillary instability.....	37
Figure 2-23: Structured micro and nanoscale spherical particles generated based on in-fiber capillary instability with isothermal heating method..	38
Figure 2-24: Applications of in-fiber generated structured spherical particles and in-fiber particles-based devices.	41
Figure 2-25: Laser recrystallization process for single crystal semiconductor optical fiber.	43
Figure 2-26: Laser-induced bandgap modification of semiconductor core fibers..	44
Figure 3-1: Simulation of capillary instability based on COMSOL.	48
Figure 3-2: Capillary instability examples in daily life.....	48
Figure 3-3: Multimaterial fiber drawing and in-fiber spherical particle fabrication.	50
Figure 3-4: Photos of spheres fabricated by laser-induced in-fiber capillary instability method.	51
Figure 3-5: Fiber drawing and redrawing.	53
Figure 3-6: Image of a fiber core breakup experiment.....	55
Figure 3-7: Breakup periods and sphere sizes with different feed-in velocity v_f ..	56

Figure 3-8: Breakup parameters based on different feed-in velocity v_f	59
Figure 3-9: Silicon nanosphere fabrication.	60
Figure 3-10: Images of Bi_2Te_3 -core borosilicate glass-cladding fiber and Bi_2Te_3 sphere produced by the laser-induced in-fiber capillary instability fabrication method.....	61
Figure 3-11: Images and characterizations of Se-core PC-cladding fiber and Se sphere produced by the laser-induced in-fiber capillary instability fabrication method.....	62
Figure 3-12: Diameter distribution of Si spheres with different feed-in velocity v_f	63
Figure 3-13: Fabrication of an array of high-Q silicon microsphere resonators for WGM excitation.	65
Figure 4-1: SnSe fiber preform preparation.	69
Figure 4-2: Fabrication of SnSe thermoelectric fiber based on fiber thermal drawing process.....	70
Figure 4-3: Mechanical properties of SnSe fiber with different diameters.	71
Figure 4-4: Schematic of laser recrystallization treatment on SnSe fiber.	72
Figure 4-5: XRD spectrum of the crystalline structures of SnSe fiber core generated on different fiber feed in velocity.....	74
Figure 4-6: Transmission X-ray diffraction of SnSe fiber core.	75
Figure 4-7: Transmission X-ray diffraction patterns of SnSe powder, as-drawn fiber and single crystal fiber after laser recrystallization.	76
Figure 4-8: XRD measurement of SnSe.	77
Figure 4-9: EBSD crystallographic map of the as-drawn fiber and after-laser-recrystallization fiber.....	78
Figure 4-10: Raman spectra of SnSe fiber with and without borosilicate glass cladding.	79

Figure 4-11: TEM observations of a single crystal SnSe fiber core after laser recrystallization.	80
Figure 4-12: Energy-dispersive x-ray measurement of element distribution in the cross-section of SnSe Fiber.	81
Figure 4-13: SnSe atomic ratio measured with EDS analysis of SnSe fiber core.	81
Figure 4-14: The schematic of TDTR system used in this work.	83
Figure 4-15: Thermoelectric properties of SnSe fibers.	85
Figure 4-16: Theoretical calculated thermoelectric properties of SnSe fibers.	87
Figure 4-17: Applications of thermoelectric SnSe fibers.	90
Figure 5-1: In-fiber material engineering system and application.	92
Figure 5-2: Systematically study of laser heating process induced phenomena based on multimaterial fibers.	92
Figure 5-3: 130 μm silicon spherical particles and stress patterns around silicon spherical particles observed in the microscope with cross-polarizers.	97
Figure 5-4: Raman shift comparison between the released silicon spherical particles and the particles in the fiber cladding.	99
Figure 5-5: (a) Emission of SnSe and silica during the laser recrystallization process and (b) related simulation of the temperature profile.	102
Figure 5-6: Plateau-Rayleigh linear instability theory model.	103
Figure 5-7: Curve of $(1-(x)^2)\Phi(x)$ with $\mu_{\text{inner}}/\mu_{\text{outer}}=0.91$	105
Figure 5-8: Viscosity ratio of copper and silica (solid black line, left axis) and the amplification ratio of wavelength and fiber core diameter (solid blue line, right axis).	106
Figure 5-9: Simulation of the amplification ratio r_{am} as a function of fiber feed-in velocity v_f by laser-induced in-fiber capillary instability.	108
Figure 5-10: In-fiber nano/micron spherical and acicular particles fabrication based on laser-induced in-fiber capillary instability.	109

Figure 5-11: Movement of in-fiber silicon micron spherical particles based on a laser trapping process..... 110

Figure 5-12: In-fiber laser trapping for multimaterial particles for designed structure fabrication..... 111

Chapter 1 Introduction

1.1 Background and Motivation

Techniques for fabricating multimaterial and multifunctional fibers through preform-to-fiber thermal drawing processes have been rapidly developed over the past decade. As compared to optical fibers, which are widely used in today's communication, great potentials of these novel fibers have been seen in their recent demonstrations of optical[1], electric[2], energy generating and harvesting[3], as well as biomedical applications[4]. The thermal drawing approach enables us to embed multiple types of material, such as metal, semiconductor, insulator, doped glass, and functional polymer, into one fiber to achieve fiber-based devices with high-level of integration. Thus, fibers could perform more functionalities than transmitting light. These novel fibers are named as multimaterial multifunctional fibers, which are also favored by their infinite length, extra flexibility, low manufacture cost, and the possibility to be used in bio-implantation. So far, plenty of multimaterial fibers and their applications have been demonstrated such as photonics bandgap fiber, optoelectrical fiber, energy harvesting fiber, and in-fiber chemical synthesis, etc.

Nevertheless, most multifunctional fibers are held in a typically axially-invariant core/cladding structure without sophisticated ways to modify material properties, which limits the multifunctional fibers to benefit from the fast-growing materials technology or to be further applied into wider areas. It is generally believed that the continuous development of multifunctional fibers requests more types of advanced materials with preferable properties to be implemented or directly fabricated in the fiber, such as extremely low-loss optical materials for opto-communication fibers and high energy-transferring efficient materials for fiber sensors or generators. Besides, developing highly-integrated fiber-based devices desire ingenious structures in both fiber cross-section axial and length axial to achieve composite functions. Consequently,

innovative approaches to precisely pattern the internal micro/nano-structure of fiber and to direct conduct in-fiber materials engineering are of the greatest importance.

Efforts have been made in recent years for developing viable methods to fabricate structures of functional materials as well as to engineer fiber materials properties to create more types of functional fibers. Methods like optical treatment[5], chemical treatment[6], mechanical treatment[7] and thermal treatment[2, 8-11] of fiber are investigated by researchers, which capably modifies either the in fiber structures or fiber materials properties or both in one method.

Among all these methods, thermal treatment, based on flame heating, oven heating or laser heating over fibers, has been gaining increasing attention and showing plenty of promising applications, such as in-fiber spherical particles generation and optical fibers fabrication with crystalline functional materials. Not only increasing the local temperature of fiber, but the thermal treatment on the fiber also induces several interesting phenomena that can be utilized for developing novel multifunction fibers such as built-in stress, Plateau-Rayleigh capillary instability, laser-induced recrystallization, and laser trapping. Through these phenomena, the original cylinder core/cladding structure of a fiber can be modified with more degrees of freedom to offer an opportunity of re-constructing the fiber structure, which is hardly performed on solid phase fiber materials. In the meanwhile, the thermal treatment enables a dramatic changing of fiber materials mechanical/chemical properties. The high temperature circumstances of interactions between materials make the modification of materials properties easy since it is more convenient and efficient to manipulate physical conditions within a small volume of fiber. So far, the potential of in fiber thermal treatment has been seen with several remarkable breakthroughs in the fabrication of functional devices in fiber, such as low-loss single crystal silicon optical fiber [1] and optoelectrical fiber [2].

Unfortunately, these existing in-fiber thermal treatment approaches are facing several challenges: (1) a wide, unstable and uncontrollable heating profile under conventional heat sources, (2) limited functional materials types that are available for the thermal treatment due to the nature of heating source and (3) lacking of theoretical analysis and study to explain complicated in fiber phenomena and reactions. These

challenges lead two problems to be still unsolved. First, despite the myriad of available thermal treatment approaches, scalable and precise fabrication methods that can produce functional particles and structures in a full range of diameters from micro-scale to nano-scale out of a wide range of functional materials have not been achieved. Secondly, most in-fiber materials engineering processes are applied solely for optical semiconductor materials, such as silicon and germanium, while the question that whether this approach can be applied to other functional materials remains unclear. What's more, several fantastic in-fiber phenomena are recently observed with the in-fiber thermal treatment being tested on multimaterial fiber, such as stress building on fiber materials and optical trapping of small objects in the melted fiber, but they are not comprehensively studied theoretically or experimentally yet. Analysis of these newly observed phenomena in the thermal treatment of fibers could be a chance to improve the existing in-fiber functional structure fabrication and material engineering method for providing more variables.

To break through these fundamental limitations of traditional in-fiber thermal treatment, we develop a new thermal treatment system based on the laser-induced in-fiber heating process. To achieve a much more controllable heating profile in the thermal treatment, we select CO₂ laser with narrow operating wavelength, small beam size, highly stable output, and precisely tunable power as the heat source. Cooperating with a fiber feed-in system, we provide an ease-of-implementation way to precisely control the in-fiber fluid dynamics and thermodynamics. Using the setup, we develop novel techniques and successfully fabricate several in-fiber micro/nano structures as well as modify fibers material properties. All fabrication methods and material engineering approaches begin with preparing a macroscopic composite multi-material solid-state preform then it is drawn into a fiber that precisely defines the initial conditions for the process. We aim to develop methods that are compatible with more functional materials as possible for making them into multimaterial fibers. It is then followed by the laser heating process thereby we can induce built-in stress, Plateau-Rayleigh capillary instability, laser recrystallization, and laser trapping accordingly at the heterogeneous interfaces along the entire length of fiber.

1.2 Objectives

In this thesis, we aim to develop and validate precisely controlled in-fiber laser-based thermal treatment platforms coupled with a sequence of universal in-fiber micro/nano particles fabrication and a method for direct in-fiber material engineering. We aim to apply these methods into the fabrication of multifunctional fiber devices with high-level of integration, tremendous flexibility, biocompatibility, and implantability. The main objectives of our works are:

- a) To develop a precisely controlled in-fiber micron and nanoscale spherical particle fabrication approach for various materials based on CO₂ laser-induced in-fiber capillary instability, aiming for achieving in-fiber multifunctional structures and fabricating high-quality micron and nanoscale spherical particles in metal, semiconductor, and functional polymer.
- b) To devise a universal approach for fabricating single crystal fiber based on the CO₂ laser-induced recrystallization process, aiming for achieving multimaterial fiber with single crystal fiber core to enhance crystal fiber's performance in optical, electric, thermoelectric and renewable energy fields.
- c) To systematically study the in-fiber CO₂ laser heating process and several laser-induced interesting phenomena, including built-in stress, material recrystallization, in-fiber capillary instability and laser trapping. We aim to achieve an in-fiber fabrication and material engineering technique that modifies the crystal structure and the electric bandgap of fiber materials, as well as manufactures in-fiber multifunctional particles and structures based on a comprehensive understanding of them.

1.3 Major Contributions

The novelty of the studies and my main contributions to this thesis include:

- a) Develop a precisely controlled and universal in-fiber fabrication approach for in-fiber micron and nanoscale spherical particles based on the CO₂ laser-induced in-fiber capillary instability. In this study, an in-fiber CO₂ laser heating system is designed, which can be applied in metal, semiconductor, chalcogenide glass and functional polymer fibers with their fiber materials melting temperature from 400 K to 2400 K and 10 orders of differences in fiber core/cladding viscosity ratio. Next, an in-fiber micro/nano spherical particles fabrication approach based on the laser-induced in-fiber capillary instability is studied. The characterization showed a highly uniform diameter, an ultra-smooth surface, and crystalline structure of these fabricated spheres. The silicon-based whispering-gallery mode resonators fabricated by this approach can achieve the Q factor as high as 7.1×10^5 .

- b) Devise a thermoelectric single crystal SnSe fiber production process based on CO₂ laser-induced in-fiber recrystallization for achieving flexible and wearable thermoelectric fibers with high thermoelectric efficiency. In this study, thermoelectric fiber with SnSe core and borosilicate glass cladding is fabricated. Then an in-fiber CO₂ laser heating system is applied, and we achieve a long-last SnSe core fiber with single crystal structure in Fm $\bar{3}$ m cubic rock-salt phase. Characterizations to demonstrate the single crystal structure of SnSe are performed. The ZT value (a dimensionless thermoelectric figure of merit) was improved from 0.58 to 1.94 at 862 K. We also develop new fiber structures with multiple fiber cores and variable diameters to achieve more applications. These results promise a new high-efficient single crystal energy harvesting fiber for the large-area applications and wearable thermoelectric devices.

- c) Construct an in-fiber CO₂ laser thermal treatment system for in-fiber integrated structure fabrication and material engineering. we study and analyze the in-fiber built-in stress, laser recrystallization, in-fiber capillary instability, laser trapping and systematically and theoretically. By controlling the laser heating temperature, cooling rate, and fiber feed-in velocity, we achieve in-fiber single crystal growth and electric bandgap modification, as well as functional particles

fabrication with precisely designed structure and distributions. In addition, we also study how these two impact factors affect the laser induced heating process in fundamental by theoretical modeling and software simulations to investigate the thermodynamic and microfluidic process.

1.4 Organization of the Thesis

In Chapter 2, we will give a general description of multimaterial fiber fabrication methods, and briefly discuss the recent progress and applications of multifunctional fibers. In addition, we introduce recent developments in methods for in-fiber micron /nanoscale structure fabrication and materials engineering.

In Chapter 3, starting from an experimental observation that a melted continuous fiber core cylinder transferred into an ordered array, we develop a method to fabricate precisely controlled scalable spheres inside a fiber based on laser-induced in-fiber capillary instability. The sphere diameter distribution, surface roughness and crystal structure of these spheres are characterized. Furthermore, we achieve a high-quality whispering gallery mode resonator based on the silicon sphere fabricated from this method.

In Chapter 4, we attain the single crystalline thermoelectric semiconductor fiber with laser recrystallization process and demonstrate the vastly improved ZT value from 0.58 to 1.94 at 862 K. We fabricate a thermoelectric SnSe fiber by the traditional thermal drawing process and then we introduce a laser heating process to directionally melt and recrystallize the SnSe fiber core into single crystal in $Fm\bar{3}m$ cubic rock-salt phase. We also characterize the single crystal structure and thermoelectric properties of the SnSe fiber. In addition, we develop a structured fiber with multiple fiber cores and variable-diameters for more widespread applications.

In Chapter 5, to further understand and extend the in-fiber laser-heating induced phenomenon, we study and analyze the in-fiber capillary instability, laser recrystallization, laser trapping, and in-fiber built-in stress systematically. With the increase of laser heating temperature and cooling rate, laser heating process will induce variable phenomena into in-fiber multifunctional materials. By using these interesting

natural physical phenomena, we achieve techniques for in-fiber controllable crystalline structure transformation, particles fabrication, and material optical and electrical properties engineering. From fundamentals, we investigate the thermodynamics and microfluidics of the in-fiber CO₂ laser heating system by mathematical modeling and software simulation.

In Chapter 6, we briefly address some future works and the main challenges for improving laser-heating-based in-fiber fabrication and material engineering.

Chapter 2 Literature Review

2.1 Introduction

When we look back to human history, the invention of fabrics plays an indispensable role in human developing. Evidence can be seen from man-made cotton fabrics dating back to 4000 BC [12] to synthetic polymers in the 20th century. With the evolution of fabric materials from cotton, wool, Nylon, polyester to advanced materials emerging in recent years, most manufactured fabrics are still made from a single material and their functionalities are depending on native properties of these materials which they are made from, including mechanical, chemical, electrical and optical properties.

Meanwhile, the 20th century witnessed the emerging and high-speed development of another type of fiber for telecommunications: the optic-fiber. In 1966, Charles K. Kao introduced a cladding-core structure glass fiber serving as an optical waveguide [13]. He was awarded the Nobel Prize in Physics in 2009 by the Royal Swedish Academy of Sciences for this groundbreaking invention. For the first time, the cladding-core structured fiber was fabricated by inserting a high refractive index glass material into a low refractive index glass material, then they were heated and pulled to draw the structure into fibers. Now, this process is known as the preform-to-fiber thermal drawing process. This optical fiber with designed structures opened the door to a whole new field for next-generation telecommunication and photonics. Today, optical fibers sustain worldwide communication and have become an indispensable part of modern society.

In addition, not just for optic applications, this multimaterial fiber pathed a new way for next-generation functional fibers and fabrics for chemical, electrical and energy fields. Over the past decades, the exploration of thermal drawing process over multimaterial fiber offers a path for developing material sciences into fiber technology. The idea is simple, by drawing a cladding-core structured optic fiber from varieties of

materials, multimaterial and multifunctional fibers are introduced. The combination of functional materials and well-designed structures makes fiber becoming a highly integrated platform not only for the optical application [1] but also for the electric applications[2], energy generation and collection, as well as biomedical applications[4].

In this Chapter, we will introduce the flourishing platform of multimaterial fibers by (1) preform-to-fiber thermal drawing process, and (2) the recent development of some typical multimaterial fibers and their potential applications. Furthermore, we also will discuss the development of bottleneck and the new development direction: in-fiber fabrication and material engineering.

2.2 Multimaterial Fibers

2.2.1 Preform Fabrication and The Preform-to-Fiber Thermal Drawing Processing

The thermal drawing process starts with a macroscopic preform holding designed structures such as cladding-single core structure, cladding-multicore structure, and the multilayer structure. Then the prepared preform is heated and drawn by the fiber drawing tower. These cores and layers of fiber can be selected from several functional materials, such as semiconductors, metals, chalcogenide glass, functional polymer, etc. The cladding materials support and shape the functional core materials during the thermal drawing process. Generally, there are three approaches to prepare multimaterial preform.

Rod-in-Tube Approach: The cladding-core structure is the most widely used preform structure. To achieve this structure, the *rod-in-tube approach* is commonly used. Selected functional material is inserted into a cladding material tube made from silica, borosilicate glass or polymer. These different materials are assembled through an evacuation and consolidation process in a vacuum oven. The inserted materials could be in consolidation rod or powder. The basic rule of this method is that the fiber drawing temperature of the heating source should be higher than the molten or soften temperatures and lower than the boiling temperature of core/cladding materials.

Figure 2-1: **Rod-in-Tube approach for preform fabrication of thermal drawing processing.**

Like the single core structure, multiple cores structured fiber containing high-density functional material arrays can also be achieved by the rod-in-tube approach. Instead of only inserting one rod, we stack multiple selected material rods, small tubes or the multimaterial fibers from previous thermal drawing process with a designed structure (Figure 2-2). The thermal drawing process will close the gaps between the parts and produce multicore fibers. The same step may be duplicated to achieve much complex multicore structures.

Figure 2-2: **Multicore preform fabrication based on a rod-in-tube approach for thermal drawing processing.**

Thin-Film Rolling Approach: A major branch of multimaterial fiber is made from polymer materials. The outstanding flexibility of polymer films enables another method for polymer-based preform preparation. Polymer thin film and selected

functional materials in film form could be layered and rolled into a preform, followed by a vacuum and consolidation process. In the case that selected functional material cannot be fabricated into film form, thermally evaporation or coating of these materials onto one side of the polymer film could be a viable approach, then they are rolled up into preforms. This method can achieve multi-layers structure fiber.

Figure 2-3: **Thin-film rolling approach for thermal drawing processing preform fabrication.** Adapted from ref [14]

Sandwich Consolidation Approach: The highly integrated fiber requires a multimaterial preform with precisely designed construction. In this case, rod-in-tube or thin-film rolling approaches may not satisfy all demands. Therefore, the sandwich consolidation approach is developed with higher precision in determining preform structures. As shown in Figure 2-4a, grooves with different shapes are carved into rectangular polymer bars. These grooves could help to precisely embed and locate the functional materials bar or to create a hollow core channel into preforms. These polymer bars with carved grooves and functional materials will be assembled, evaporated and thermally consolidated as a preform. This approach can achieve complicated structure fiber.

Figure 2-4: **Sandwich consolidation approach for thermal drawing processing preform fabrication.** (a) Polymer-based preform structure before consolidation. Part 1-3 are functional material bars as photodetector and electrodes. Part 4 is polymer bars with curved grooves. (b) Fiber thermal drawing process with the preform after the consolidation process. Adapted from ref [15].

Thermal Drawing Processing: After preform preparation, the preform is drawn into the fiber by the thermal drawing processing. As shown in Figure 2-5, the preform is fixed at a fiber drawing tower and heated by a cylinder furnace. First, we preheat the preform into the “drop temperature”. This temperature is decided by the softening point T_s and melting point T_m of core and cladding materials. The aim of this preheating process is to neck down the preform at a selected point. Subsequently, the bottom of preform starts falling and draws the preform down into the fiber shape under the effect of gravity. Then, instruments at the top of the tower begin to feed the preform into the furnace at a controlled velocity $v_{feeddown}$. The bottom is cut off and the fiber is fed into a cane, which pulls the fiber at a controlled velocity $v_{pulling}$. The typical fiber drawing process starts here. The fiber shares identical geometry and composition with the preform but becomes much longer. The diameter of the fiber is decided by the ratio between the feed-down velocity and the pulling velocity:

$$\frac{D_{preform}}{D_{fiber}} = \sqrt{\frac{v_{feeddown}}{v_{pulling}}} \quad \text{Eq.1}$$

The fiber drawing tower also equips with auxiliary equipment to monitor the drawing process. Two sets of laser diameter-measurement gauge continuously measure the fiber diameters with and without coating. A tensiometer is used to measure the tension in the

fiber during the drawing process, which is highly necessary because setting a suitable drawing tension can help to avoid the breakage of the fiber. This drawing tension can be adjusted by changing the heating temperature and pulling speed. If the tension is too high, we can raise the heating temperature and reduce the pulling speed. With a group of applicable factors (furnace temperature, velocities of feed-down and pulling, etc.), one preform could be drawn into hundreds-of-meters long fiber.

Figure 2-5: **Schematic of the multimaterial fiber fabrication based on the thermal drawing process.** The preform is fed into the heating furnace at a controlled speed. The macroscopical preform is molten and drawn down to a micron fiber. The diameter of the fiber is controlled by the ratio between the preform feed in speed and the pulling speed. The insert image is the cross-section of a silicon-core silica-cladding fiber.

2.2.2 Materials Collocation and Selection

As mention in chapter 1, the thermal drawing process provides us with a platform to incorporate diverse materials into one fiber. Materials like insular-metal-semiconductors for the optoelectronic application[2, 11, 16, 17], chalcogenide glass for photonics application[18, 19], and biocompatible polymers for biomedical and biochemical application[15, 20, 21], multifunctional fibers are fabricated successfully. Due to the diversity of functional materials, the collocation and selection of materials set which can be co-drawn together is a noteworthy concern.

The main constraints in the multimaterial fiber fabrication are located on the properties of materials. The thermal drawing process heavily relies on the intrinsic characteristics of the materials, such as the viscosity η , molten/soften temperature (T_m/T_s), linear thermal expansion coefficient (LTEC) and surface tension. The wide differences in these properties over diverse materials become a grand and fundamental challenge in the multimaterial fiber fabrication.

Firstly, the cladding materials should be amorphous resisting devitrification, which can support the functional structure and maintain the preform structure during the thermal drawing process.

Secondly, the molten or glass transition temperatures of both cladding and functional materials should be located at a similar interval. Otherwise, the mismatching of heating temperature would introduce component decomposition and phase transition, which are not wanted in a fiber drawing process.

Lastly, the linear thermal expansion coefficients of involved materials should be comparable. Volume change of functional materials will introduce stress or strain over the cladding/core interface during the thermal drawing process and even after the process. Selecting a comparable LTECs can prevent the breakages and cracks in fiber cladding during the fabrication process.

To meet these requirements simultaneously, appropriate sets of cladding materials and functional core materials are chosen, and they show a path to the fabrication of multimaterial fibers. Polymers, borosilicate glass, and silica are the three most commonly used cladding materials at the present. According to properties of these three cladding materials, functional materials can also be divided into three groups: a high-temperature group that prefers silica as the cladding, middle-temperature group

that prefers borosilicate glass as cladding and low-temperature group that prefers polymer as cladding.

Figure 2-6: **Dynamic viscosity, melting/glass transition temperature and the linear thermal expansion coefficient of selected materials.** (a) Viscosity versus temperature of Polymer (Polycarbonate[22]), chalcogenide glass (Se[23]), borosilicate glass[24], thermoelectric material (Bi_2Te_3 [25]), silica[26], metal (Au, Cu [27, 28]) and semiconductor (Si, Ge [29, 30]). (b) The melting temperature of metals, semiconductors, and thermoelectric materials and the glass transition temperature of polymer, chalcogenide glass and silica plotted against the linear thermal expansion coefficient (LTEC [14]) of selected materials.

Table 1: Dynamic Viscosity and Melting/Glass

Cladding / Core Materials	Melting or Glass Transition Temperature (T_m or T_g)	Linear Thermal Expansion Coefficient ($10^{-6}/K$)
PC	420 K (T_g)	65
Borosilicate Glass (BK7)	830 K (T_g)	7.1
SiO ₂	1986 K (T_g)	0.6
Se	494 K (T_m)	37
Bi ₂ Te ₃	853 K (T_m)	13.8
Ge	1211 K (T_m)	6.2
Au	1337 K (T_m)	14.2
Cu	1357 K (T_m)	16.6
Si	1687 K (T_m)	3

2.3 Multifunctional Fibers

With the rapid development of the multimaterial fiber, the macro-to-micro fiber thermal drawing method plays a more and more important role in arranging areas. The functional materials with optical, electronic, acoustic and thermoelectric properties can be combined into one multifunctional fiber. A wide range of integrated fiber-formed devices has been developed based on this approach. These in-fiber devices work as sensors (light, acoustic wave and heat), transmission mediums (not only for optical signal but also for electric, acoustic and biological signals) or generators based on piezoelectric, thermoelectric and triboelectric effects, etc. What's more interesting and promising about this methodology is its potential to use these fibers as textiles. Knitting these fibers into multifunctional textiles, we can see the potentials to enable traditional fabrics with more functions. This section will focus on the recent progress in these developing technologies.

2.3.1 Photonics Bandgap Fibers

Photonics bandgap (PBG) fibers have a hollow core surrounded by two-materials multilayers structure. PBG fiber is one of the early developed multimaterial fibers [31]. An omnidirectional mirror that can reflect light coming at any angle is lined on the inner surface of the hollow core fiber. Therefore, the PBG hollow fiber could serve as axial light guidance. Plenty of applications have been developed based on PBG:

Transmission of high-power laser: High power laser, no matter in outputting pulses or continues waves, is of foremost value for many applications (medical, industry, military and bioscience). Nevertheless, the existing silica-based optical fiber is not suitable for developing laser because of its strong absorption of light energy. PBG hollow core fibers have been proven to be a good waveguide for high-power laser owing to its multimaterial omnidirectional mirror structure. PBG hollow core fiber has transmitted peak power of 11.4 MW at 1.55 μm with 97% at the output [32] and high-power continuous wave (CW) CO₂ laser at 10.6 μm [31]. In addition, the transmission fibers for laser at 350 nm and 750 nm can also be achieved by different multilayer structure designs[33] (Figure 2-7).

Figure 2-7: **SEM images of PBG fibers cross-section for high-power laser transmission.** (a) Polymer-composite PBG fibers for transmitting high peak power pulse laser at 1.55 μm . (b) The transmission spectrum of hollow core PBG fibers for high power CW laser at 10.6 μm . (c) Wavelength scalability of hollow core PBG fibers. Transmission spectra of four fibers with peak wavelengths at 350 nm, 750 nm, 1.55 μm and 10.6 μm . The transmission peak could be controlled by the period of the multilayer structure of the fibers. Adapted from refs [31-33].

Azimuthally polarized radial lasing fibers: The hollow core of a PBG fiber is also an ideal architecture for radially emitting fiber lasers: the hollow core can provide a host for a gain medium and the multimaterial layers lining the inner surface become a Bragg structure. More specially, the emitting light direction of hollow-core PBG fiber is not limited to fiber-end emitting as other kinds of fiber lasers do, surface-emitting of the laser is possible where the gain medium is located. These unique emission characteristics provide more possibilities for developing fiber laser applications[34]. Several gain mediums of radially emitting fiber laser have been tested: organic dye dissolved in a solid host, organic dye solution[14, 35, 36] and CdSe/CdZnS/ZnS quantum dots (QDs) solution[37] (Figure 2-8). In these cases, the gain mediums are placed in the hollow core and pumped axially. The radiation pattern by the solid host is anisotropic, while the radiation pattern by the solution is symmetric.

Figure 2-8: **Azimuthally polarized radial lasing fibers.** (a) Schematic of the emitting fiber laser with organic dye (solid host and solution) as gain mediums. (b) Schematic of the emitting fiber laser with QDs solution as a gain medium. Adapted from refs [14, 35-37].

In addition, the direction of emitting-laser could be precisely controlled by introducing two oppositely facing liquid-crystal microchannels. Rotations of the liquid-crystal molecule could be controlled by applying an electric field above the threshold voltage. The optical anisotropy and spatial orientation of liquid-crystal molecules provide the possibility to modify the emission laser polarized state passing through microchannels.

Figure 2-9: **Liquid-crystal directional emission control of an azimuthally polarized radial lasing fiber.** (a) Schematic of the hollow core PBG fiber with two oppositely facing liquid-crystal microchannels. (b) Emitting laser spectra transmitted. Adapted from refs [36].

Chemiluminescent trace vapor sensing fibers: By coating chemiluminescent dye into the hollow core, the PBG fiber has been demonstrated as a chemical trace vapor sensor. The chemiluminescent dye reacts with the trace vapor and emits light, which is transmitted through the same fiber to the analyzer. The chemical trace vapor sensor showed the sensitivity in ppm level [38].

Figure 2-10: **Chemiluminescent vapor sensing based on PBG fibers.** (a) Schematic of the principle of chemiluminescent detection based on a hollow core PBG fiber. (b) The PBG fiber transmission bandgap and chemiluminescent emitted light. (c) Sensitivity measurement (fiber length: 58 mm). Adapted from ref [38].

2.3.2 Optoelectrical fibers

Nowadays, integrated optoelectrical devices have wide applications. However, traditional wafer-based optoelectrical devices may not be suitable for some applications due to their rigid and inflexible structures. Making flexible integrated optoelectrical fiber a viable option for several circumstances.

Figure 2-11: **Optoelectrical integrated fiber devices.** (a, c, d, f) SEM micrographs of various of optoelectrical fibers. (b) Photodetecting fiber for resolving optical illumination distributions. (based on the fiber structure shown in figure a. (e) Large-scale optical-field measurements with the optoelectrical fiber shown in figure c and d. (g) Single grid lensless imaging based on the optoelectrical fiber shown in figure f. Adapted from refs [16, 17, 39-44].

Multimaterial fiber's thermal drawing process makes it possible to integrate metals, insulators and semiconductors in a well-designed fiber structure. Following this idea, a series of optoelectrical fibers has been achieved (Figure 2-11 a, c, d and f) [16, 17, 39-43]. The basic working mechanism of optoelectrical fibers is to transfer the optical signals and optical power into electrical signals. For example, in order to improve the performance of the optoelectrical fiber, in-fiber semiconductors are patterned into thin film form, which greatly reduces the dark current. Therefore, it also reduces the noise level. Meanwhile, the thin film structure also provides the possibilities to integrate devices with higher density in one fiber. For example, the fiber structure shown in Figure 2-11f achieved higher device density than that in Figure 2-11d. Another important advantage of optoelectrical fibers is its large-scale integrability. The flexible optoelectrical fibers could support for hyperfine 2D or 3D structures.

These fibers have been demonstrated with a variety of remarkable applications, which can help to resolve the optical illumination distributions along fiber [43]. Besides, lensless imaging [41], thermally and optically sensor array [39, 44] have been reported recently.

2.3.3 Energy Harvesting fibers

Flexible and wearable energy harvesting devices have been deeply and comprehensively studied during the past decades [45-47]. As for energy harvesting, fibers based on piezoelectricity, thermoelectricity and triboelectricity materials are attracting more and more attention due to its flexibility in fabrication and using.

Piezoelectric fibers: The piezoelectric material is a kind of energy harvesting materials based on the piezoelectricity, which generates electric charges in response to applied mechanical stress [48]. Piezoelectric materials have been widely used in various areas, such as harvesters[45], biosensors[49] and acoustic sensors[50-52]. To achieve large-scale flexible and wearable piezoelectric acoustic sensor device, the piezoelectric materials are incorporated into multimaterial fibers to enable self-powered sensing functionalities on these fibers [53-55].

The acoustic wave lases the piezoelectric fiber and places stress on the functional materials, which subsequently transfers forces into electrical signals without connecting bias. The signal can be easily recorded and processed by an electrometer.

For example, after signal processing (Fast Fourier Transform), the piezoelectric fiber can measure the intensity and the frequency of differentially multiple acoustic waves. with a 0.01 MHz detection resolution [53].

Furthermore, by constructing the piezoelectric fibers into a 3D array networking sensor, acoustic positioning is successfully demonstrated. As shown in Figure 2-12c, the intensities of voltages from 6 fibers could position the acoustic wave source.

Figure 2-12: **Schematics and operating principle of piezoelectric fibers.** (a) Schematic showing the structure and thermal drawing process of a rectangular piezoelectric fiber. (b) Schematics and SEM image of a cylindrical piezoelectric fiber with an integrated Fabry-Perot cavity structure. (c) Schematic of a 3D underwater acoustic sensor network based on rectangular piezoelectric fiber array. (d) Near-field pressure patterns of the acoustic emission from a circular, triangular and rectangular fiber. The cross-section dimensions of these fibers are around 2 mm. Adapted from refs [53-55].

Thermoelectric fibers: Thermoelectric (TE) materials have the intrinsic capacities of realizing the mutual transformation between thermal energy and electric power. Therefore, TE devices become one of the most promising ways for energy harvesting [56-58]. Developing a new architecture is an important path to exploit high energy consumption applications of thermoelectric devices with high energy conversion efficiency. Traditional TE devices are made mainly of crystalline block materials, which are rigid and heavy. Although there is some solution for making flexible TE devices, such as coating TE materials on textiles or forming organic conducting polymers, the output power density and mechanical stability remain to be improved [46, 59-63].

Figure 2-13: **Schematics and operating principle of thermoelectric fibers.** (a) Schematic showing the structure and thermal drawing process of thermoelectric fiber. (b) Thermoelectric fibers are woven into clothing as a wearable thermoelectric device. (c) Photo and SEM image of flexible thermoelectric fiber. (d) Schematic and demonstrated thermoelectric fiber-based pipe. This setup measured the output voltage as a function of the temperature difference generated by hot/freezing water. The inset of d shows the FEM-simulated maximum output power of the thermoelectric tube with the different quantities of thermoelectric p-n pairs at the temperature difference of 40 K. Adapted from ref [64].

Developing TE fiber is an approach to achieve flexible and wearable TE devices with the high output power density and good mechanical stability in an ease-of-fabrication way [64]. This TE fiber is constructed by the borosilicate glass as cladding, the most commercially TE material, Bi_2Te_3 , as the n-type core, and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ as the p-type core [65]. A polymer coating with $\sim 100\text{ }\mu\text{m}$ thickness is applied on the TE fiber to guarantee its mechanical robustness during using. Another notable advantage of using TE fiber is that long and flexible TE fiber can be attached closely to heat sources with irregular and curved shapes, e.g., the human body, water pipe and cup. Studies on TE fiber have shown that thermoelectric generators based on this TE fiber could provide mW cm^{-2} -level output density.

Triboelectric Fibers: Triboelectric effect is a phenomenon based on two materials contact electrification and static induction when charged materials are moving away from each other, which is discussed to be viable electrical energy that can be harvested by human beings. However, the working principles of this mysterious phenomena are still cannot be completely explained but the energy harvesting process can be well explained with Maxwell's displacement current equation [66, 67]. While the understanding of the fundamental principle remains to break through, the triboelectric effect has been widely used for energy harvesting and multifarious sensors with very impressive self-powered performance. Triboelectric nanogenerator (TENG) is an energy harvesting device that can effectively derive energies [68-71]. Dr. M. Bayindir and his group developed TENG fibers as a power harvesting and biochemical sensing device with polysulfone (PSU) cladding and poly(vinylidene fluoride) (PVDF) core [3] (Figure 2-14). The principle of this TENG fiber devices is explained as shown in Figure 2-14: the droplets introduce electrical potential changes on the electrode when passing through. The intensity and frequency of the voltage peaks represent the volume and flowing velocity of droplets. This technology opens a path for in-fiber neural detection and cell analysis, it is worth to note that, the fiber is working without any power sources such as batteries or external wires, making it possible to developing wearable or implantable fiber sensors, which are short of energy sustained supplying methods today.

Figure 2-14: **Schematics and operating principle of triboelectric fibers.** (a) Schematic showing the structure and thermal drawing process of triboelectric hollow core fiber. (b) Schematic and demonstrated triboelectric hollow core fiber-based power harvesting and biochemical sensing. (c) Working Principle of triboelectric fiber device based on TENS. Adapted from ref [3].

2.3.4 In-fiber Chemical Synthesis

The fiber thermal drawing process provides high temperature and vacuum environment in a very confined space, which could be an ideal environment for synthesizing some chemicals. What's more, the fiber drawing process could be a high-throughput in-situ chemical reactive carrier. The fiber thermal drawing process leads to the phase change on the core materials, followed by the chemical reactions. New compounds are produced by chemical reactions or by element diffusions during the phase change[72].

Crystalline silicon core fibers fabrication: The crystalline silicon core fibers are fabricated from a preform without any elemental silicon[6]. The preform consists of aluminum (Al) core and silica cladding. The melting temperature of Al is 660.32 °C and the drawing temperature of silica fiber is around 2200 °C. During the thermal drawing process, Al is melted and oxidized by the surrounded silica (SiO_2). This chemical reaction produces silicon atoms and alumina (Al_2O_3). Because the fiber drawing temperature is higher than the melting temperature of both Al and Al_2O_3 , the formation of Al_2O_3 shield can be thereby avoided. As the reaction going on, the excessive Al_2O_3 precipitates out from the molten Al, while Si stays whining the molten Al. With smaller densities than Al_2O_3 , the molten Al and Si would float up and let Al_2O_3 sink down. Ultimately, this reaction consumes all Al and leaves highly pure Si inside the fiber.

Figure 2-15: **Crystalline silicon core fiber fabrication and forming mechanism.** (a) The chemical reaction of Al and silica at the core and cladding interface. (b-e) The Al_2O_3 precipitates out and sink down to the bottom and highly pure silicon is obtained. Adapted from ref [6].

ZnSe core fibers fabrication: Like the crystalline silicon fiber fabrication process, the thermodynamic in-fiber compound synthesis process produces fibers with Zinc selenide (ZnSe) core. ZnSe is a widely used direct bandgap semiconductor material thus making ZnSe core fiber be of great importance in development semiconductor materials fiber [73, 74]. However, due to the high molten temperature of ZnSe (1530 °C), the direct fabrication of ZnSe fiber from ZnSe preform under standard fiber thermal drawing process is not viable. To overcome this challenge, in-fiber synthesis of ZnSe core from in-fiber chemical reactions provides a new solution.

The ZnSe core fiber could be fabricated in the standard fiber thermal drawing setup to allow reactions between $\text{Sn}_{85}\text{Zn}_{15}$ and Se_{97}S_3 happening *in situ* [72]. A similar method was developed based on the in-fiber reactions between Zn and Se_{97}S_3 [75].

Figure 2-16: **ZnSe core fiber in situ fabrication based on in-fiber synthesis.** (a) Schematic ZnSe fiber fabrication based on in-fiber synthesis ($\text{Sn}_{85}\text{Zn}_{15}$ and Se_{97}S_3). (b) Schematic ZnSe fiber fabrication based on in-fiber synthesis (Zn and Se_{97}S_3). Adapted from refs [72, 75].

In situ alignment of carbon nanofiber: Implantable microelectrodes based on carbon nanofibers provide a feasible way to investigate brain activities by recording and transmitting neurons electric signals. Using fiber thermal drawing process, a biocompatible polymer cladding fiber with a carbon nanofiber electrode could be made [21].

Figure 2-17: ***In situ alignment of carbon nanofiber fabricated by a thermal drawing process.*** The carbon nanofiber could transfer electrical neural signal and be biocompatible neural probes. Adapted from ref [21].

It is worth mentioning that carbon nanofibers with random orientations inside the preform are reoriented and aligned *in situ* by the elastic field from the polymer matrix along with the extension. After the alignment, the carbon nanofibers are in the same longitudinal direction, which helps to provide a stable electrical recording of electric signals during brain activities.

2.3.5 Highly-Integrated Fiber-based Devices

As shown in the last few sections, multimaterial fiber and thermal drawing process could be a great platform to embed various materials with different properties, such as photoelectricity, electrical conductivity, energy harvesting, and bio/chemical sensing. Hereby, multimaterial fiber-based devices show enormous potential for all-in-fiber sensors[15], labs-on fiber[76], probes[20] and functional textile[77, 78]. Figure 2-18 shows some highly integrated multi-material fiber-based devices. Here, three successful attempts are discussed.

Firstly, multimaterial fiber is an ideal platform for neural studies because of its small size, flexibility under mechanical forces, biocompatible if fabricated with polymers and capability to be integrated with sensing components, making it possible to implant these fibers into the brain for neuron signal detection. The neural signal generated from brain function includes simultaneous electrical, chemical and mechanical signals[79]. Simultaneous probing of neurons is indispensable to understand the fundamental working principles and pathologies of many neurons systems. Increasing numbers of researches are focused on optogenetics [80-82]. For a remarkable example, Prof. Yoel Fink and his group developed a novel fiber probe that allows simultaneous optical stimulation, neural electrical signal recording, and drug delivery to be operated inside a mice brain. This fiber is fabricated based on a thermal drawing process[20]. As shown in Figure 2-18 a, the multimaterial fiber probe is consisted by 1) a conductive polyethylene (CPE) core as an electrode, 2) a polycarbonate (PC) core as an optical signal transmission channel, 3) rectangular hollow channels as drug delivery channels, and 4) a polycarbonate (PC) tube as cladding. The transmission spectroscopy of this probe is in visible wavelengths that range from 400 nm to 700nm, which contains the activation wavelength of channelrhodopsin 2 (ChR2) (473 nm). The *in vivo* experiment showed that neural

activities corresponded to laser stimulations were observed. Furthermore, optically evoked activities were also observed which were responses related to successful drug-delivery. Last but not the least, good biocompatibility of the fiber probes has been proven during the *in vivo* experiment, ensuring the safety of using this fiber.

Secondly, fiber-based chemical sensing is emerging based on multimaterial fiber [15]. In recent decades, optical fibers have shown widespread applications as chemical sensors [83-89]. Among these applications, luminescence-based fibers attracted increasing attention for their abilities to collect and transmitting the emissive signal of chemicals [90, 91]. This all-in-fiber chemical sensing technique requires a highly-integrated multimaterial fiber that works based on the luminescence effect. A typical structure of this fiber is consisted of 4 parts, as shown in Figure 2-18 c: (1) a Se_{97}S_3 layer as emitted light detector, (2) $\text{Sn}_{63}\text{Pb}_{37}$ as electrodes, (3) a conductive polycarbonate (CPC) pads as the link, and (4) a polysulfone (PSU) matrix as the host cladding. Furthermore, the designed larger rectangular hollow core in the center of the fiber serves as an azimuthal numerical aperture, this design helps to significantly increase the emitted chemiluminescent light detecting efficiency. This fiber-based sensor has been demonstrated as a trace-level detector that sensitively detects peroxide vapor down to 10 parts per billion. Even more noteworthy is that a large-scale fiber sensing array for chemical could be achieved by this all-in-fiber structure further enhance its sensitivity (Figure 2-18 d).

Furthermore, wearable fabric woven with diode fiber has also gained much attention with several important works reported [78]. There is no doubt that semiconductor diodes and LEDs have become indispensable parts of modern communication, computation and life [92]. The diode fiber developed a textile-form wearable diode fiber for the very first time. So far, two types of diode fibers are created: light-emitting diode fiber and photodetecting diode fiber. The design of each diode fiber is shown in Figure 2-18 e. Two tungsten microwires are converged into polycarbonate cladding and a few semiconductor devices are embedded. During the thermal drawing process, the tungsten microwires with a high molten point will not be molten but packaged together as electrodes. The electrodes are well-designed to touch the contact pads of semiconductor devices.

Figure 2-18: **Multimaterial integrated fiber-devices.** (a) Preform and cross-section images of multifunctional fiber. This fiber is designed to test the neural response in vivo for optical signal, electrical and chemical interrogation. (b) Multimodality probes were implanted into mice. (c) Schematic of preform and cross-section of all-in-fiber chemical sensing. The chemical sensing fiber is consisted by (1) Se_{97}S_3 layer, (2) $\text{Sn}_{63}\text{Pb}_{37}$ electrodes, (3) CPC pads, (4) PSU matrix. (d) Schematic of the principle of all-in-fiber chemical sensing. Slots are introduced through the fiber cladding to a large-scale fiber array for chemical and optical signal collection and measurement. (e) Preform, cross-sections and SEM images of diode fibers. (f) Diode fibers with embedded electronics which are so flexible and woven into wearable fabrics. Adapted from refs [15, 20, 77, 78].

Wearable applications of this kind of diode fiber have been demonstrated such as bi-directional optical communication link with receiver and emitter fibers and heart-rate measurements. The textile-grade diode fiber could ensure proper operation even after several machine-wash circles.

2.4 In-fiber Micro and Nanoscale Structures Fabrication

As the fiber thermal drawing process could transfer macro preform into micron and nanofibers, it paths a new way for micro-and nanoscale structures fabrication that is compatible with various materials and completed in a standard thermal drawing process. This fabrication approach could be considered as a marriage of two research fields: multimaterial fiber technology and micro/nano technology. Recently, nanotechnology has provided many opportunities in diverse areas [93-96], such as size-dependent optical excitation, microelectronics, information storage, biotechnologies, and life sciences.

considering the special advantages of multimaterial fiber, it is feasible to develop a novel precisely controlled, repeatable and stable fabrication approaches for micro/nano objects with delicate structures. By inserting macro functional materials rod into the preform and then drawing it into the fiber, micro and nanowires could be fabricated simply. Indeed, several breakthroughs in micro and nanoscale structures fabrication have been made based on fiber thermal drawing process, such as micro/nanowires of metal, semiconductor and chalcogenide glass have been successfully achieved. From another perspective, the ability to fabricate functional micro/nano structures in-fiber also opens a new path of multifunctional fiber to in-fiber multifunctional device fabrication and broadens its applications.

Furthermore, as an interesting experimental phenomenon, in-fiber capillary instability was also observed during fiber thermal drawing process and post thermal heating process. The thermal heating process which melts the fiber core and softens the fiber cladding induces fluidic instability at the interface between core and cladding. The surface tension at this interface introduce perturbation wave and lead the continuous fiber core to move and breakup into a string of spheres to reduce the surface

energy. The ability to fabricate in-fiber spherical structures paths a way of micro/nano precision manufacturing.

Here, we will introduce the state-of-the-art of in-fiber micro and nanoscale structures fabrication methods and their successful applications.

2.4.1 In-fiber Micro- and Nanowires Fabrication

Many techniques have been developed to produce nanowires. In this section, we will discuss fabrication techniques based on the thermal drawing process with more extensive details. Generally, there are two methods to fabricate micro/nanowires in fiber. One is based on the in-fiber fluid instability, another is based on a multiple-times thermal drawing process.

Figure 2-19: Breakup of multilayers into nanoscale structure based on fluid instability during multimaterial fiber thermal drawing process. (a) Schematic of a preform with multilayer structure. Fiber cross-section indicates that the thinner layer of functional material breakup into nanowires by spinodal instabilities. (b) SEM image of the observation of inner layer breakup phenomenon. (c) Se/PSU fiber cross-section SEM image showing that the breakup threshold thickness is 100 nm. (d) Magnification As₂Se₃/PES fiber cross-section showing that the threshold is 15 nm. Adapted from ref [97].

First, we start from the approach based on in-fiber fluid instability. During the thermal drawing process of multilayer fibers, researchers have noticed that breakups occurred over some extremely thin films. One reasonable explanation is that spinodal instabilities will impact the resulting lay geometry while the preform is heated to fluid state as shown in Figure 2-19. Therefore, the duplication of multilayer has been studied over and been finely controlled to fabricate micro/nanowires during the fiber thermal drawing process.

Secondly, there is another fabrication method based on the two-time thermal drawing. As mentioned in section 2.2.1, the rod-in-tube preform preparation approach could be repeated two times or even several times. Using this approach, we could fabricate preform with a bundle of functional material cores which brings multicore fibers. For the second way which is based on a multiple-times thermal drawing process shown in Figure 2-20, the microstructure of functional material rods could be achieved by a one-time thermal drawing process from a macron preform. Then the bundles of manicured micron rods are embedded into a new preform for the second-time thermal drawing process, which eventually produces nanowires of functional materials. The size of the nanowire is determined by the number of repeating times of the thermal drawing process.

Figure 2-20: **Fabrication of in-fiber nanoscale structures based on the thermal drawing process.** The microscale functional material rods could be fabricated from the first thermal drawing process. A bundle of manicured functional material rods can be thermally drawn to nanoscale by a second-time thermal drawing process. Adapted from ref [98].

As shown in Figure 2-21, numerous kinds of nanowires have been developed based on these two methods from microscale to several nanometers [97-99]. These ordered nanowires share the exact same diameters and endless lengths. They can be embedded in cladding materials for enhanced environmental stability or etched out for other applications. This powerful method offers exciting opportunities for micro/nanoscale devices fabrication with no limitations in devices' length. Furthermore, complex in-fiber structures are compatible with this approach. Unsymmetrical and anisotropic in the cross-section direction of preform also could be achieved as shown in (Figure 2-21 d).

Figure 2-21: **Characterization of fabricated nanowires.** (a) SEM images of orders As_2Se_3 nanowire arrays from 570nm, to 200 nm to 100nm. (b) High-density As_2Se_3 nanowire arrays of 20 nm diameters. (c) As_2Se_3 nanowires fabricated from two-times thermal drawing process. (d) The fiber of dual-thickness layers. The fiber cross-section shows the fidelity of a thicker layer and breakup of the thinner layer. Adapted from refs [97-99].

2.4.2 In-fiber Micro- and Nano-Spherical Particles Fabrication Based on Capillary Instability

As mentioned in the last section, the breakup of the core was observed during the thermal treatment of fibers [100, 101]. Actually, the breakup not just happened on multilayer structures, but also on cylinder cores. During the thermal drawing process, the macron preform is heated and its material would transform into viscous liquid status. Researchers have observed that the surface tension between core and cladding materials will lead the cylinder core to breakup into a series of spheres. These spheres share the same diameter and structure. For multimaterial fiber fabrication, this

phenomenon will lead the functional core to be noncontinuous and shall be avoided. However, multimaterial fiber researchers have viewed this capillary instability induced breakup phenomenon as paths to new ways of generating micro and nano structures.

The physical theory and the influencing parameters of the observed breakup phenomenon are studied comprehensively. The post process of thermal heating is introduced after the fiber thermal drawing process. As shown in Figure 2-1 and Figure 2-22 a, the multimaterial fiber with a continuous core is inserted into a furnace, which applies a thermal gradient at the fiber and transforms the fiber core/cladding materials into viscous liquid status. At the interface of viscous core and cladding, the Plateau-Rayleigh instability will dominate due to the surface tension. This fluid instability phenomenon will induce a sinuous perturbation at the interface, which will develop and increase to break the continuous fiber core. The fiber core will transform into a chain of spherical particles with the same diameter and shape. The physical phenomenon of Plateau-Rayleigh instability will be discussed in detail in the following chapters. Here, we will briefly introduce several successful studies for generating in-fiber micro and nanospheres.

Thermal treatment on fiber is the key to transfer the multimaterial fiber into the viscous liquid status and it initiates the in-fiber capillary instability. Traditional thermal treatment methods are to heat the multimaterial fiber in an oven or a furnace under selected temperatures. This in-fiber particles generation approach has three notable features. First, it can help to fabricate a large amount of uniformly sized spherical particles (Figure 2-23)[102]. Second, the generation of in-fiber particles is scalable and repeatable that is the particles could be generated from the same structured fiber under controlled parameters. The most important advantage is the capacity to generate structured and multifunctional micro and nanoscale spheres from functionalized materials. This capacity comes from several aspects: doping material, diversity of sphere structures, and spheres coating materials.

Figure 2-22: **Size-controllable spherical particle generation based on in-fiber capillary instability.** (a) The schematic of a multimaterial preform is thermally drawn into a fiber and thermal processing of the fiber induces the in-fiber capillary instability. (b) Optical micrograph of an As_2Se_3 core fiber cross-section with the 20-mm-diameter core; inset shows the core (scale bar, 20 mm). (c) Microscope images of the fiber side-view in b after an oven-isothermal heating treatment is applied to induce the Plateau-Rayleigh instability. (d) Calculated instability time as a function of fiber core diameter and heating temperature. (e) SEM images of microparticles. (f) SEM images of nanoparticles. Adapted from ref [102].

As shown in Figure 2-23 b, with a doping material, the in-fiber generated spheres gain more functionalities such as emitting fluorescence [103]. While coating the spheres with antibodies or antigens would make these spheres useful in immunoassay [103]. The ability to generate diversities in spheres structure is of more interest. As shown in Figure 2-23 d-h, core-shell spheres, Janus, “beach ball” spheres and micro/nano-capsule spheres were achieved by the structured core multifunctional fibers. Notably, even much complex particles structure may be generated by ingeniously structuring the multimaterial fiber core.

Figure 2-23: **Structured micro and nanoscale spherical particles generated based on in-fiber capillary instability with isothermal heating method.** (a) SEM micrograph of a large amount of 40 μm diameters of As_2Se_3 spherical particles released from fibers. (b) Fluorescing photographs of laser dye-doped COP core fiber and generated spherical spheres. The laser dye-doped spheres could be made to fluorescing in the red, blue or green. (c) Schematic of COP spherical particles after treatment with poly-L-lysine. These particles are coated with FA1 and then FA3 [anti-goat antibodies produced in donkey (dAg), which recognize FA1]. (d) Schematic, microscope image and SEM micrograph of the generation of core-shell (As_2Se_3 -PES) structure spherical spheres. P, polyether sulfones (PES); G, As_2Se_3 . (e) Schematic, microscope image and SEM micrograph of the generation of core-shell (COP-PC) structure spherical spheres. (f & g) Schematics and EDX spectrum images of preforms and generated Janus and “beach ball” particles fabrication. G1, As_2Se_3 ; G2, $(\text{As}_2\text{Se}_3)_{99}\text{Ge}_1$; P, PES. (h) Schematic and microscope images of microencapsulation of biological materials in polymer shells. (Scale bars: 20 μm). Adapted from refs [98, 102, 103].

Based on the ability of a scalable and size-controlled generation of particles, the in-fiber spherical particle fabrication approach is of significant technological and scientific importance. Here, we will introduce some applications based on semiconductor fiber and chalcogenide glass fibers.

First, a series of silicon-in-silica PN molecules is achieved by this technology[8]. Due to the completely melted status during fiber thermal drawing process, the contact of p-type and n-type semiconductor cores is not possible. Separated dual-core semiconductor fibers with one core in p-type core and another core in n-type are fabricated as instead. The micro/nano spherical particles in fiber generation based on Plateau-Rayleigh instability bring a new way to in-fiber PN molecule fabrication. As shown in Figure 2-24a, the dual-core silicon fiber is thermally heated and transferred into viscous liquid status. Then the induced surface tension at the interface between silicon and silica destroys the continuous of dual cores and leads the cores to break up into two chains of spheres. It is worth mentioning that the diameter of spheres is larger than the diameters of dual-core, which lets the two chains of spheres contact with each other, resulting in a PN molecule. To avoiding the mixture between n-type and p-type materials, a new heating method, gradient thermal heating which is achieved by using a flame, is invited. The gradient thermal heating method provides a limited heating zone to effectively avoid the unwanted mixture of two materials.

Second, optoelectronic fibers can also be fabricated based on the selective amplification of in-fiber capillary instability[8]. Based on a precisely defined metal-semiconductor-metal tri-cores fiber, a fully functional optoelectronic in-silica device is achieved by employing Plateau-Rayleigh instability in fiber. As mentioned in the last section, the thermally heating process will transfer the functional material into a viscous liquid statue and lead the continuous core breakup into a chain of spheres. Differ from transferring all cores into spheres, only semiconductor core (Germanium) breaks into a chain of spheres because of the distinct melting points between Germanium and Platinum. The Ge spheres with larger diameters would contact the continuous Pt metal cores directly and form a fully functional in-fiber optoelectronic device.

Furthermore, spheres fabricated from this method features ultra-smooth surface roughness owing to surface tension and large built-in stress [9, 104, 105], which is an extraordinary platform for developing optical resonators. Therefore, the micron and nano-spherical particle generation based on in-fiber capillary instability open a new route for fabricating chalcogenide microcavity resonator arrays[9]. In general, a chalcogenide glass material, As_2Se_3 , is made into the rod and is drawn into the fiber with PES cladding material by a thermal drawing process. Following by the isothermal heating process, the continuous chalcogenide glass core breaks into a chain of spheres due to the in-fiber Plateau-Rayleigh instability. These spheres have an ultra-smooth surface, perfectly spherical shape and uniformly diameters, which consisted a 3.1×10^5 high-Q factor whispering gallery mode (WGM) chalcogenide microresonator array. Furthermore, this fabrication method based on in-fiber capillary instability can be expanded to be applied on As_2Se_3 , semiconductors (Si and Ge) and silica.

The in-fiber generated structured functional spherical particles has made considerable progress and development. Many applications have been achieved based on this technology. However, some challenges are still existing. The isothermal heating method by oven or furnace will induce the satellite spheres (Figure 2-22c, smaller spheres) between the main spheres, which will reduce the uniformity of spheres diameter. Meanwhile, the gradient heating method still lacks the ability to provide a precisely controlled heating zone. A new method is needing to overcome these obstacles which we will discuss in Chapter 3.

Figure 2-24: **Applications of in-fiber generated structured spherical particles and in-fiber particles-based devices.** (a) Schematics, photos and experiment resulting in the synchronous breakup of a dual-core silicon fiber and generation of PN molecule based on in-fiber capillary instability. (b) Fiber cross-section, spheres generation and experiment resulting in optoelectronic fibers based on multimaterial fiber and optoelectrical devices generated by in-fiber capillary instability phenomenon. (c) SEM images and transmission spectrum of chalcogenide glass whispering gallery mode sensor arrays based on the As_2Se_3 spherical particles generated by in-fiber capillary instability. Adapted from refs [2, 8, 9].

2.5 In-fiber Materials Engineering

With the fast-developing of multimaterial fiber, an increasing number of multifunctional fibers based on functional materials have been studied. As mentioned in the previous sections, photonics bandgap fiber, optoelectrical fiber, energy harvesting fiber and highly-integrated fiber-based devices serve wider roles in our societies. However, a major factor that has limited the practical application of these fibers is how to achieve crystalline structures in these functional materials for better material properties. Previous studies have shown that functional materials embedded in fibers are in mostly amorphous or polycrystal structure after fiber drawing process [8, 54, 106, 107]. These discontinuous crystal structures introduce perverse effects on the optical and electronic properties, such as higher optical transmission loss [10], lower electrical transport properties, lower energy conversion efficiency and larger lattice thermal conductivity[108]. Therefore, tremendous efforts are being spending on in-fiber material engineering, attempting to modify the material properties especially the crystal orientation of materials.

2.5.1 Laser Induced Recrystallization for Single Crystal Fiber Fabrication

One of the most important approaches of in-fiber material engineering is to achieve laser assisted recrystallization of fiber materials, which produces high-quality single crystal functional fiber. Recent researches of in-fiber recrystallization are focusing on the optical semiconductor fibers to achieve low transmission loss infrared optical fiber [10, 11, 109, 110].

There are two typical approaches to product optical semiconductor fibers: (1) high-pressure chemical vapor deposition (HPCVD) of functional materials inside glass capillaries[111, 112], and (2) thermal drawing fibers from a functional material-core, glass-cladding preforms [1, 16, 113-115]. The functional core of the fiber, during the thermal drawing process, will be molten to liquid and then solidify and crystallize rapidly forming a polycrystalline structure. So far, the reported optical transmission losses of the semiconductor optical fiber leave space to be improved due to the impurities and cracks at the polycrystal grain boundaries.

To reduce the grain boundaries of polycrystal fiber cores, laser heating processing is introducing to modify semiconductor optical fibers. As shown in Figure 2-25, to alter the polycrystalline or amorphous fiber core into a single crystal structure, a laser-induced recrystallization process is designed. A stable laser beam helped to heat a limited zone of the fiber core and to scan the whole fiber which is similar to the zone-melting single crystal growth method [116]. The movement of the narrow molten region melts the polycrystalline material at its forward edge and leaves a single crystalline material behind it. By modifying the laser scanning velocity and heating temperature, a suitable single crystal growth rate could be established. Low transmission loss single crystal silicon core fiber [10, 110], germanium core fiber, GaSb core fiber [117], and SiGe core fiber [109] have been realized.

Figure 2-25: **Laser recrystallization process for single crystal semiconductor optical fiber.** (a) Schematic of the recrystallization process by scanning the semiconductor optical fibers with a laser as a heating source. (b) Transmission windows of some infrared core materials for the semiconductor optical fiber. Adapted from ref [110, 113].

2.5.2 Extreme Electronic Bandgap Modification in Multimaterial Fibers

Another important direction of in-fiber material engineering is material bandgap modification [5, 109, 118]. For decades, silicon, as a representative of semiconductor materials, shows excellent optical properties in the near and mid-infrared wavelength. To apply the silicon fiber to work for a broader detecting light wavelength spectrum, modification of bandgap on semiconductor fibers is essential.

Recent studies have shown the possibility for bandgap modification in semiconductor fibers. During the thermal drawing process for semiconductor fiber, gigapascal-level built-in stress is induced onto the semiconductor fiber cores [119, 120], which will change the lattice spacing, as well as the electronic bandgap. The built-in stress on the semiconductor cores is believed to be a result of the volume mismatching between the glass cladding and semiconductor cores. Therefore, the laser recrystallization process could be used in precisely controlling the growth of the crystal and then modifying the bandgap of semiconductor cores.

Figure 2-26: **Laser-induced bandgap modification of semiconductor core fibers.** (a) Schematic of laser induced bandgap modification process. The CO₂ laser is used as a heating source and ZnS lens are used as a focus lens. (b) Raman spectrum of silicon core fiber with bandgap modifications. According to the shipment of Raman spectrum peaks, the bandgap of silicon core is reduced from 1.11 eV to 0.59 eV. Adapted from refs [5, 109, 118].

2.6 Summary of Chapter 2

We have presented the relevant history and background information of multimaterial and multifunctional fiber, including the basic definition, common fabrication methods, current development status, and potential applications.

However, most current applications of the multimaterial fiber are based on original as-drawn fiber after the thermal drawing process without any post-processing approach. The original fiber after the thermal drawing process has a simple axial structure and defective functional material structure. Therefore, many post-processing processes, such as in-fiber particles and structures fabrication, as well as in-fiber materials engineering based on laser-induced thermal treatment, is highly desired. We

will move to the discussion from traditional in-fiber fabrication and material engineering methods to a laser-based precisely controlled thermal treatment. And we will expand the material engineering postprocessing to more types of multimaterial fibers.

Chapter 3 In-fiber Particles Fabrication Based on Capillary Instability

3.1 Introduction

The need for scalable fabrication of spherical particles at both micro- and nano-scales is well-documented, and achieving this enables a variety of applications ranging from microelectronics[121], photonics[122], healthcare[123], biology[124], chemical sensing[125], to cosmetics.

To date, both top-down[126] and bottom-up[127, 128] methods to fabricate such particles have been intensively developed, but they cannot seamlessly link the full spectrum of sphere radii. Moreover, the existing scalable fabrication approaches of particle synthesis involve specific material systems and commonly result in narrow ranges of applicable sizes that strongly depended on the chemistry and growth kinetics dictated by these processes. This sort of process cannot be readily expanded to other material systems or extended to larger particle sizes because of limitations imposed by mass transport, agglomeration, capping groups, and kinetics of particle growth[129-131]. On the other hand, conventional microfluidic-based approaches are able to produce nanoparticles by chemical synthesis, but the size of produced particles is limited in nanoscale. Also, it is hard to produce size-homogenous particles due to the difficulties in controlling the reactions. Despite the myriad of available approaches, a fundamental challenge remains to develop a scalable and precise fabrication method that is able to fabricate spherical particles in a full range of diameters from micro-scale to nano-scale out of a wide range of functional materials.

Here, we report a new fabrication method to produce uniformly-sized, high-quality, and globally ordered spherical particles. As an ideal heating source in fiber's thermal treatment due to its narrow operating wavelength, small beam size, highly stable output and precisely tunable power, the CO₂ laser is used in our work to control

the in-fiber fluid dynamical unstable area. The demonstrated fabrication method begins with a macroscopic composite multi-material solid-state preform drawn into a fiber that defines precisely the initial conditions for the process. It is then followed by laser heating to fluidize the fiber thereby inducing the PR capillary instability at the heterogeneous interfaces along its entire length. As the resulting sphere size is mainly determined by the fiber core diameter, this fabrication method seamlessly links the fabrication of spherical particles in a full spectrum of diameters from micro-scale to nano-scale. More importantly, this dynamic process provides a generic solution to achieve sphere fabrication from a variety of materials with disparate optical, electronic, and thermoelectric properties with a wide range of processing temperature from 400 K to 2400 K and 10 orders of difference in fiber core/cladding viscosity ratio regardless of the crystal structures. Furthermore, we demonstrate the application of fabricated high-quality silicon microspheres as whispering-gallery mode (WGM) resonators with the Q factor as high as 7.1×10^5 .

3.2 In-fiber Capillary Instability

3.2.1 Introduction to Capillary Instability

The classical capillary instability describes a cylindrical liquid to break-up into a train of spheres under the surface tension at the interface. This phenomenon is perhaps one of the most ubiquitous fluid instabilities. As shown in Figure 3-1, when a fluid inkjet is surrounded by another kind of liquid or air, the surface tension will induce a sinusoidal perturbation at the interface of two materials and lead the cylinder to break-up into droplets in a sphere shape with the development of the perturbation wave amplitudes.

This phenomenon frequently appears in daily life [132]. For example, the faucet dripping, the ink-jet printer system, and the wine tears on the glass are all typical capillary instability phenomena.

Figure 3-1: **Simulation of capillary instability based on COMSOL.** A small perturbation in the cylindrical fluid interface develops and results in break-up into a train of spheres. (a-d) The process of instability development by time.

As a common physical phenomenon, the study of capillary instability has a very long history. In 1849, Joseph Plateau proved experimentally that a vertically falling water column would break-up into some drops which have the same volume. Then, J. Plateau explained this phenomenon with an analysis of surface tension in balance. The reason for the break-up process to occur is also due to its result that can reduce the surface energy until the establishment of an equilibrium situation.

Figure 3-2: **Capillary instability examples in daily life.** (a) the wine tears in the glass. (b) the faucet dripping. Adapted from ref [MIT 1.63 Lecture Notes on Fluid Jets,” *MIT Lecture Notes*, no. Figure 1, pp. 1–8, 2011.].

Later, Lord Rayleigh studied the phenomenon theoretically by applying a linear stability analysis. His study showed that the break-up of a vertically falling water

column needed to satisfy two conditions. Firstly, the falling water column will break-up into some drops if the length of the column exceeds its circumference. Secondly, the drops result from some small disturbances that develop with time[133-135].

Subsequently, Tomotika found the viscosities ratio between two kinds of materials, such as liquid-in-liquid or liquid-in-gas, are critical factors of the capillary instability. At the same time, he furthermore improved Lord Rayleigh's linear instability theory. By the separation of time and space, he described that the development of small disturbance is affected by a factor named instability growth rate. This model also offers possibilities for conducting a numerical simulation to analyze the capillary instability[136]. Based on Tomotika's theory and related mathematics models, many addition phenomena have been inquired deeply [13, 132, 137]. It is worth to mention that the theory is also proved to be solid in sub-micron scale [138]. We will discuss these theories in detail in Chapter 5.

3.2.2 Thermal Treatment Induced In-Fiber Capillary Instability

Although not being found on solids, the capillary instability takes place in molten multimaterial fibers. Due to the surface tension and viscous dissipation force between the molten fiber cladding and core[139], the core cylinder breaks up and results in a string of spheres that are frozen *in situ* upon cooling. As introduced in Chapter 2, the recent study on in-fiber capillary instability phenomenon has led to the development of fabrication and material engineering inside a fiber, especially for the fabrication of microspheres[101, 140], which is strongly related to the Plateau-Rayleigh (PR) capillary instability in a fiber. Fabrication of microspheres has been achieved based on fluidizing the pre-fabricated fibers either by the isothermal heating via furnace[9, 141] or the axial thermal gradient heating via oxyhydrogen flame[8].

However, these approaches are facing several challenges to produce uniformly-sized and high-quality spherical particles:

- (1) wide and uncontrollable heating profiles;
- (2) unavoidable satellite spheres generation[9];
- (3) limited material selections due to the nature of these heating sources;
- (4) high core-to-sphere amplification ratio due to the large heating area.

These challenges have essentially limited their studies and applications. To break these limitations, a new fabrication method is needed, which shall be based on the following aspects:

- (1) The heating profile should be precisely controllable;
- (2) Gradient heating method to avoid satellite sphere generation;
- (3) Adjustable heating temperature to fit various functional materials;
- (4) The limited heating area to reduce the core-to-sphere amplification.

To meet these requirements, we developed a gradient heating system with a CO₂ laser as the heating source.

Figure 3-3: **Multimaterial fiber drawing and in-fiber spherical particle fabrication.** Schematic of multimaterial fiber thermal drawing process. The inset shows the formation of spheres based on the in-fiber capillary instability.

3.3 Laser Induced In-fiber Capillary Instability

3.3.1 Background Information

Here, we report a new laser-based method of thermal treatment to produce uniformly-sized, high-quality, and globally ordered spherical particles. CO₂ laser is an ideal heating resource due to its narrow operating wavelength, small beam size, highly stable output and precisely tunable power, which can heat and fluidize the fiber thereby induce the PR capillary instability. This fabrication method seamlessly links the fabrication of spherical particles in a full spectrum of diameters from micro-scale to nano-scale by parameter adjustment. More importantly, this dynamic process provides a generic solution to achieve sphere fabrication from a variety of materials with disparate optical, electronic, and thermoelectric properties with a wide range of processing temperature from 400 K to 2400 K and 10 orders of difference in fiber core/cladding viscosity ratio regardless of the crystal structure.

Figure 3-4: **Photos of spheres fabricated by laser-induced in-fiber capillary instability method.** The sphere sizes range from 250 μm, 180 μm, 90 μm, 12 μm, 950 nm, to 200 nm.

3.3.2 Fiber Fabrication

To start, distinct groups of multimaterial fiber are obtained from the thermal drawing approach, as illustrated in Figure 2-6. A preform with core-cladding structure is prepared first. The target core materials (solid rod or powders) are inserted into a tube made of cladding materials, this rod-in-tube approach is introduced in Chapter 2.

By feeding the preform into a furnace under a controlled speed, the preform can be drawn into fiber when the temperature is above both the melting point (T_m) of the core material and the glass transition point (T_g) of the cladding material. Considering the difference of T_m , T_g and thermal expansion coefficients (TEC) (Figure 2-1) among materials as well as the construction of fiber preform, we categorize typical functional materials into three distinct groups: high temperature group (cladding: silica; core: Si, Ge, Au, and Cu), medium temperature group (cladding: borosilicate; core: Bi_2Te_3), and low temperature group (cladding: polymer; core: Se and chalcogenide glass). These fiber core materials cover most commonly used materials in photonics[142], electronics[20, 143], optoelectronics[2, 144] and thermoelectric applications[145, 146]. Note, the drawing temperatures of these groups range from 400 K to 2400 K, and the viscosity ratios between the fiber core and fiber cladding vary from 10^{-3} to 10^{-12} (Figure 2-6).

Four groups of multimaterial fibers are fabricated. The fabrication of the silicon-core silica-cladding fiber and the selenium-core polycarbonate-cladding fiber is presented here. The other two groups of preforms are fabricated in a comparable way. For the silicon-core silica-cladding fiber, fused quartz tubes and rods (Scott Glass Products) and silicon rods (Lattice Materials 99.99%) are used. The structure of the preform is shown in Figure 3-5. A silicon rod with 2 mm diameter is inserted into the fused quartz tubes with the inner diameter of 2 mm and the outer diameter of 16 mm. The preform is drawn at 2100 °C with the feed-in speed of 0.6 mm min⁻¹ and drawing speed of 0.3 m min⁻¹. This process results in a silicon-core silica-cladding fiber with the core diameter of 90 μm and the outer diameter of 720 μm. To achieve 4 μm silicon core fiber, the 90 μm silicon core fiber is fed into a new set of fused quartz tubes whose total outer diameter is 8 mm. The new preform is drawn at 2130 °C with the feed-in speed of 6 mm min⁻¹ and drawing speed of 3 m min⁻¹.

For the selenium core polycarbonate-cladding fiber, selenium powder (Alfa Aesar, 99.9999%) is firstly consolidated to a rod in a fused quartz tube (Scott Glass Products) under 280 °C. And a hole with a diameter of 3 mm and the depth of 5 cm is drilled in a polycarbonate rod (Professional Plastics Pte Ltd) with a diameter of 25 mm. The selenium rod is placed in the polycarbonate rod, further covered with polycarbonate films, and then consolidated at 190 °C under vacuum. This preform is heated to 200 °C in the top zone and to 300 °C at the bottom zone. The two-zone heating method can avoid the breakup of core and maintain its continuous shape during the drawing process. The preform feed-in speed is 1 mm min⁻¹ and the draw speed is 1.4 m min⁻¹. This process results in the selenium core fiber with core diameter of 80 μm and cladding diameter of 700 μm.

Figure 3-5: **Fiber drawing and redrawing.** (a) A 2-mm silicon rod is inserted to a set silica tube with the total outer diameter of 16 mm with a sealed bottom. The preform is vacuumed and fused on the other side. (b) Cross section of silicon fiber after fiber drawing process. The diameter of fiber core D_{core} is 90 μm and the diameter of the fiber cladding D_{cladding} is 720 μm. (c) A 10-cm silicon fiber fabricated in part a is inserted to a set of silica tubes with the total outer diameter of 8 mm with a sealed bottom. The preform is vacuumed and fused on the other side. (d) Cross section of silicon fiber after the redrawing process. The diameter of fiber core D_{core} is 4 μm and the diameter of the fiber cladding D_{cladding} is 300 μm.

3.3.3 Precisely Controlled Microscale Particles Fabrication

According to the PR instability theory[135], when a liquid cylinder is surrounded by another liquid or gas, a sinusoidal perturbation wave with wavelength λ would appear on the surface of the liquid cylinder due to the difference of surface

tension forces between the interfaces of the two materials. Tomotika's analysis[136, 147] showed that the perturbation on the interface develops exponentially with a time constant

$$\tau = D_{\text{core}} \mu_{\text{clad}} / [\gamma(1-x^2)\Phi(x, \mu_{\text{core}}/\mu_{\text{clad}})] \quad \text{Eq. 2}$$

where $x = D_{\text{core}}/\lambda$, μ_{core} , μ_{clad} are the viscosity of the fiber core and cladding materials; γ is the interfacial surface tension between two materials, and Φ is a defined function[148]. The perturbation will lead the liquid cylinder to break up into a chain of spheres. The growth rate of the perturbation and the breakup timescale is decided by the viscosities of fiber core and cladding materials. Based on the in-fiber capillary instability, several sphere fabrication methods have been reported[8, 9, 101, 140, 141].

For example, a multimaterial fiber is placed in an isothermal environment to allow the uniform heating on the entire length of fiber core[2, 9]. Thereafter, the core softens and breaks up into a chain of self-assembled spheres whose sizes are determined by the original fiber core sizes and by-product satellite spheres. However, some fundamental limitations still exist. The first limitation is the large perturbation wavelength λ , which remains in a high order thus resulting in a large amplification ratio r_{am} between the sphere diameter D_{sphere} and the original fiber core diameter D_{core} , described as:

$$r_{\text{am}} = D_{\text{sphere}}/D_{\text{core}} \quad \text{Eq. 3}$$

As a result, the large amplification ratio r_{am} would increase the complexity and difficulty in fabricating very thin fibers in order to further achieve nano-scale spheres using the isothermal fabrication method. Another unavoidable limitation in the isothermal method is to precisely control the resulting sphere sizes, as the isothermal break-up process constantly leads to the formation of satellite spheres, which is still a complex route to be controllable[149, 150]. On the other hand, axial thermal gradient heating by oxyhydrogen flame[8] shows a way to avoid the formation of satellite spheres, but the narrow operating temperature window further limits the selection of materials that are applicable to such an approach.

To address these limitations, our solution is to feed the resulting multimaterial fiber through a CO₂ laser beam at a precisely-controlled feed-in velocity v_f . Thanks to the small heating area under the laser beam, only a short section of fiber is heated to reach the temperature that is enough to melt both the fiber core and cladding. Then, a perturbation occurs at the molten core/cladding interface, leading to the transformation from a continuous cylinder to a chain of spherical particles with uniform diameters, as experimentally observed in Figure 3-6. More importantly, by changing the feed-in velocity v_f , spheres with different diameters can be fabricated from the same fiber, thus the amplification ratio r_{am} can be controlled. Furthermore, this method offers a stable and widely tunable in-fiber temperature profile by adjusting the radiation power of CO₂ laser according to the actual absorption ratio of different materials. To study this process in detail, we firstly analyze the influences of laser power on the in-fiber temperature with commercial simulation software (COMSOL). Fiber feed-in velocity v_f , CO₂ laser radiation power, and fiber cladding material are considered as the variables in the heating process, as illustrated in Figure 3-8b. In the COMSOL simulation model, CO₂ laser beam sweeps the silica fiber, borosilicate glass fiber, and polycarbonate fiber at 6.5 W on silica, 6 W on silica, 2.5 W on borosilicate, and 1W on polymer respectively with different fiber feed-in velocities ($10 \mu\text{m s}^{-1}$ to $100 \mu\text{m s}^{-1}$). The laser spot size is set to be $300 \mu\text{m}$ which is comparable to the diameter of these fibers. Simulation results clearly show that CO₂ laser is capable to provide sufficient heating power for all three distinct groups of materials, and the tunable heating temperature lays the foundation for the universality of our fabrication method to various functional materials.

Figure 3-6: **Image of a fiber core breakup experiment.** Using a 4- μm silicon-core silica-cladding fiber heated by a 6.5 W CO₂ laser under the feed-in velocity v_f of $10 \mu\text{m s}^{-1}$. The breakup period is $75.5 \mu\text{m}$ and the resulting sphere diameter is $12 \mu\text{m}$.

Therefore, the heating system is built with a 20 W CO₂ laser (Diamond C20) and a linear translation stage (Thorlabs LNR50S/M). The laser is focused to achieve a

minimum beam size of 150 μm with a ZnSe lens. The power of the laser is modulated by customized software and is measured by a thermal power sensor (Thorlabs S314C).

As the increasing of in-fiber temperature leads to the decreasing of viscosities of the fiber core and cladding when the feed-in velocity slows down, this fabrication method enables us a way to precisely control the sphere size by simply changing the feed-in velocities.

Figure 3-7: **Breakup periods and sphere sizes with different feed-in velocity v_f .** (a) Breakup results of an 80 μm Se-core fiber under the CO_2 laser power of 1 W. Feed-in velocity v_f : 10 $\mu\text{m s}^{-1}$, 40 $\mu\text{m s}^{-1}$, and 70 $\mu\text{m s}^{-1}$. The larger spheres are Se spheres and the smaller spheres are air bubbles. (b) Breakup results of a 20 μm Bi_2Te_3 -core fiber under the CO_2 laser power of 2.5 W. Feed-in velocity v_f : 10 $\mu\text{m s}^{-1}$, 30 $\mu\text{m s}^{-1}$, 50 $\mu\text{m s}^{-1}$, and 70 $\mu\text{m s}^{-1}$. (c) Breakup result of a 4 μm Cu-core fiber under the CO_2 laser power of 6 W. Feed-in velocity v_f : 10 $\mu\text{m s}^{-1}$, 60 $\mu\text{m s}^{-1}$, 130 $\mu\text{m s}^{-1}$, and 150 $\mu\text{m s}^{-1}$. (d) Breakup result of a 4 μm Si-core fiber under the CO_2 laser power of 6.5 W. Feed-in velocity v_f : 10 $\mu\text{m s}^{-1}$, 30 $\mu\text{m s}^{-1}$, 50 $\mu\text{m s}^{-1}$, and 70 $\mu\text{m s}^{-1}$.

Figure 3-7 shows the relationship between feed-in velocity v_f and the diameter of formed spheres for four typical multimaterial fibers: (1) Si-core SiO_2 -cladding fiber

(high temperature group), (2) Cu-core SiO₂-cladding fiber (high temperature group), (3) Bi₂Te₃-core borosilicate glass-cladding (medium temperature group), and (4) Se-core PC-cladding fiber (low temperature group). These fiber materials cover typical semiconductor, electric, thermoelectric, and chalcogenide glass. Moreover, these four kinds of spheres empower wide applications and great potentials in photonics sensing[151], microelectronics[143] and thermoelectric modules[148, 152]. The statistics of break-up period λ shows that with a slower feed-in velocity v_f , the sphere pinch-off occurs deeper into the heating area, which results in a larger sphere diameter D_{sphere} . Note that, the small spheres appear near Se and Bi₂Te₃ on the Figure 3-7 are not satellites, they are confirmed to be some air spheres. Some air holes will stay in the fiber and breakup into some air holes under the laser heating process together with the core materials. These air bubbles can transfer light, so their centers are lighted up.

As shown in Figure 3-8, we summarize the experimental results of the amplification ratio r_{am} for these four material groups as a function of feed-in velocity v_f in a steady heating state, in which the r_{am} of laser-based approach is significantly reduced than that of previously reported. As the spot size of CO₂ laser can be as small as 100 μm , this method offers a small confined heating area in fiber. Therefore, much less core material can be involved in each sphere's formation, achieving the smallest amplification ratio to release the fabrication challenge for the generation of uniformly sizes nanospheres. The confined heating area in fiber and the dynamic heating process also eliminate the appearance of the satellites. More importantly, with the outstanding stability of laser power, the average standard deviation value (SD) of the fabricated sphere diameters is smaller than $\pm 3\%$ of the average sphere diameter (see Figure 3-12 for the distribution of sphere diameters). Note that this small size variation is also caused by the small change of fiber core diameter induced within the fiber drawing process. A smaller standard deviation value can be achieved by a more uniform fiber core via the further optimization of the fiber drawing process. Therefore, our laser heating method is advantageous over the previously reported approaches with the merits of much smaller amplification ratio and more precise controlling of the sphere diameters.

The saturation of the size effects is observed as the velocity goes from 10 to 20 $\mu\text{m s}^{-1}$ on Cu/Silica group. By simulation study on the laser induced in fiber

temperature, we indicate that the change of temperature at velocities 10 and 20 $\mu\text{m s}^{-1}$ is not obvious. The almost unchanged temperature can be the reason for the saturation of the sizes. For the saturation of Si/silica group, we can observe that the in-fiber temperature just above the melting temperature of silicon at the feed-in velocity of 70 $\mu\text{m s}^{-1}$ in Figure 3-8. The low-temperature threshold is the reason for the weak.

Furthermore, according to the Tomotika model which indicates that the breakup period is decided by both the materials viscosities and heating temperature. Based on material viscosities, the core-cladding sets can be categorized into high-viscosity set and low viscosity set. Comparing with low-viscosity sets such as Silicon-Silica and Cu-Silica, the high-viscosity sets such as Se-PC and Bi_2Te_3 -Borosilicate glass has a large instability growth rate and a longer breakup time scale. From the other side, the temperature ranges of Se and Bi_2Te_3 are also smaller than Si and Cu.

Figure 3-8: **Breakup parameters based on different feed-in velocity v_f .** (a) Experimental results of the amplification ratio as a function of the feed-in velocity v_f for selected multimaterial fibers. (b) Simulation results of laser-induced temperature in fiber under the feed-in velocity v_f from $10 \mu\text{m s}^{-1}$ to $100 \mu\text{m s}^{-1}$. The CO_2 laser power is 6.5 W for silicon-core silica-cladding fiber, 6 W for copper-core silica-cladding fiber, 2.5 W for borosilicate glass-cladding fiber, and 1 W for polycarbonate-cladding fiber.

3.3.4 Spheres Fabrication down to Nanometer Scale

In addition, our method features with wide scalability in sphere fabrication as demonstrated in

Figure 3-4. Diameters of fabricated spheres ranging from hundreds of micrometers to nanometers are successfully achieved. Considering the breakup wavelength limitation as $\lambda = \pi D_{\text{core}}$ in PR instability phenomena, a nanometer scale core

is required to achieve the fabrication of nano-scale spheres, thus a multiple-step size-reduction process is developed.

Figure 3-9: **Silicon nanosphere fabrication.** (a) Photograph of the fiber redraws process. The silicon fiber core is redrawn from 4 μm to 350 nm. The fiber feed-in speed is $v_1 = 10 \mu\text{m s}^{-1}$ and the fiber drawing speed $v_2 = 1.44 \text{ mm s}^{-1}$. (b) SEM image of a 4 μm silicon core released from the fiber before the redraw process. (c) SEM image of a 350 nm silicon core released from the fiber after the redraw process. (d) SEM image of a chain of silicon nanospheres released from the redrawn fiber. The inset shows silicon nanospheres with diameters of 950 nm, 420 nm, and 200 nm.

Taking Si/silica fiber for instance, after the initial fiber drawing mentioned above to obtain a silica-cladding fiber with a Si-core of 90 μm in diameter, this fiber is inserted into another silica tube to run through the same thermal drawing process, which ends up with a Si-core fiber with 4 μm core diameter (see Supporting Information Figure S1 for details). Then, referring the similar fiber drawing method, this 4 μm Si-core fiber is fed into CO₂ laser beam at a slow speed ($10 \mu\text{m s}^{-1}$) and drawn at a fast speed (1.44 mm s^{-1}) from the other end (Figure 3-9 a). The tapering process further scales the fiber by a factor of 12 while keeping a continuous Si core with a diameter of $330 \pm 20 \text{ nm}$ (Figure 3-9 b and c). This fiber is then fed into the laser beam at $10 \mu\text{m s}^{-1}$ for spheres fabrication, while the laser spot size is 300 μm and power is 7 W. Fabrication of Si sphere with the diameter of 950 nm is achieved using this protocol. Lastly, the Si spheres are released from silica by hydrofluoric acid (HF) etching of fiber cladding. The released sphere chain is imaged by the scanning electron microscope

(SEM) as shown in Figure 3-9 d. With the same process, Si nanospheres with diameters of 400 nm and 200 nm can also be achieved (Figure 3-9 d insets).

3.4 Characterization and Size Distribution of Generated Spheres

To characterize these spheres (Si, As, and Bi_2Te_3) from our developed fabrication method, scanning electric microscope (SEM), X-ray diffraction (XRD), and Atomic force microscopy (AFM) is being used.

Figure 3-10: Images of Bi_2Te_3 -core borosilicate glass-cladding fiber and Bi_2Te_3 sphere produced by the laser-induced in-fiber capillary instability fabrication method. (a) Cross section of Bi_2Te_3 -core borosilicate glass-cladding fiber. The diameter of fiber core D_{core} is 20 μm and a diameter of fiber cladding D_{cladding} is around 300 μm . (b) SEM image of a single Bi_2Te_3 sphere with the diameter of 54 μm . The sphere is fabricated under 2.5 W CO_2 laser power and feed-in velocity of 20 $\mu\text{m s}^{-1}$. (c) AFM analysis of the surface roughness of the Bi_2Te_3 sphere. The mapping area is $1 \times 1 \mu\text{m}$ and the root-mean-square (RMS) roughness is $< 2.8 \text{ nm}$. (d) XRD spectrum of the Bi_2Te_3 spheres indexed according to ICDD PDF-4+ entry no. 01-079-4904.

To observe these fabricated spheres in detail, we released them from the cladding, using hydrofluoric acid (HF) for etching silica and borosilicate glass-based fiber, and dichloromethane for dissolving polymer-based fiber. Figure 3-10b and Figure 3-11b show the SEM images of Bi_2Te_3 and Se microspheres released from fiber cladding, which indicate the perfect spherical structure and ultra-smooth surface.

Figure 3-11: Images and characterizations of Se-core PC-cladding fiber and Se sphere produced by the laser-induced in-fiber capillary instability fabrication method. (a) Cross section of Se-core PC-cladding fiber. The diameter of fiber core D_{core} is 80 μm and the diameter of fiber cladding D_{cladding} is around 700 μm . (b) SEM image of a single Se sphere with a diameter of 200 μm . The sphere is fabricated under 1 W CO_2 laser power and feed-in velocity of 10 $\mu\text{m s}^{-1}$. (c) AFM analysis of the surface roughness of the Se sphere. The mapping area is 1 $\times$ 1 μm and the RMS roughness is < 2.2 nm. (d) XRD spectrum of the Se sphere indexed according to ICDD PDF-4+ entry no. 00-006-0362.

In addition, we use XRD to investigate the crystal structure of these formed spheres. XRD spectra of these spheres indicate the crystalline structure of these spheres. Comparing with the amorphous structure, the crystalline structure shows better optical and electronic properties, which will be discussed in chapters 4 and 5. Furthermore, AFM scanning images show the ultra-smooth surface of these spheres. The mapping

area is $1 \times 1 \mu\text{m}$ and the root-mean-square (RMS) roughness of these spheres are smaller than 2.8 nm.

We also measured the diameter of Si micro particles by microscope and plot the diameter distribution in Figure 3-12. The statistics present the uniformity of particles size and supports the standard deviation values mentioned in the manuscript and the error bars in Figure 3-8 c. The size distribution of micro and nanoparticles made from other materials has similar tiny fluctuation in their measured diameters.

Figure 3-12: **Diameter distribution of Si spheres with different feed-in velocity v_f .** (a) Diameter distribution of Si spheres at feed-in velocity $v_f = 10 \mu\text{m s}^{-1}$. (b) Diameter distribution of Si spheres at feed-in velocity $v_f = 30 \mu\text{m s}^{-1}$. (c) Diameter distribution of Si spheres at feed-in velocity $v_f = 50 \mu\text{m s}^{-1}$. (d) Diameter distribution of Si spheres at feed-in velocity $v_f = 70 \mu\text{m s}^{-1}$.

3.5 Application of The Silicon Spheres Generated from The Laser-Induced In-Fiber Capillary Instability

High-Q Silicon Microcavity Resonator: We further demonstrate the use of the fabricated Si spheres as a WGM micro-resonators. WGM resonators with high-quality factor (Q) and small mode volumes are widely investigated in bio-sensing, micro-lasing, optical signal processing, and nonlinear optics. Considering the wide application of Si-based devices in micro-photonics, micro-electronics and their broad transparency window from 1.1 μm to 6.7 μm , Si resonators in different geometries have been studied in detail[153, 154]. However, it is still challenging to fabricate a high-quality three-dimensional (3D) Si-based WGM resonator or a resonators array in a simple and feasible way.

By our laser-induced in-fiber capillary instability fabrication approach, an array of Si spheres with a diameter of 60 μm is fabricated. To characterize the optical performance, a tapered fiber is used to couple light in and out of the Si sphere resonator (Figure 3-13 c). The diameter of the tapered fiber is 2 μm in the waist section, which is tapered from a standard single-mode fiber with a diameter of 125 μm . The fiber with silica glass cladding is placed in 49% hydrogen fluoride (HF) solution (Sigma Aldrich, Singapore) until the cladding material is completely dissolved. A high-resolution optical spectrum analyzer with a laser output (BOSA 800, Aragon Photonics) is used to detect the output resonance spectrum. The normalized transmission spectrum of this Si micro-resonator ($D = 60 \mu\text{m}$) is shown in Figure 3-13 d. The dips in the spectrum are the higher azimuthal order modes. Following the relationship

$$\Delta\lambda_{\text{FSR}} = \lambda^2 / (n\pi D_{\text{sphere}}) \quad \text{Eq. 1}$$

where λ is the dip position wavelength and n is the refractive index of the silicon ($n=3.48$), the theoretical FSR should be 3.72 nm. The normalized transmission spectrum of a dip located at a wavelength of 1563.34 nm is shown in Figure 3-13e. The bandwidth $\Delta\lambda$ of the dip is measured to be 2.2 pm, corresponding to a quality factor Q of 7.1×10^5 . To the best of our knowledge, this is the highest Q factor in Si spherical

resonators achieved so far (please find more detail in appendix). To gain a better understanding of the transmission spectrum of our Si sphere resonator and the parameters which affect the Q factor, we have analyzed the coupled mode theory.

Figure 3-13: Fabrication of an array of high-Q silicon microsphere resonators for WGM excitation. (a) SEM images of an array of silicon microspheres. The average diameter of silicon microsphere is $12\ \mu\text{m}$ with the standard deviation of $\pm 0.27\ \mu\text{m}$ ($\pm 2.3\%$). The inset is a single silicon microsphere with a diameter of $12\ \mu\text{m}$. (b) XRD spectrum of a $60\ \mu\text{m}$ silicon sphere, indexed according to ICDD PDF-4+ entry no. 00-005-0565. The inset is the AFM surface characterization of this $60\ \mu\text{m}$ silicon microsphere on the north polar ($1\ \mu\text{m} \times 1\ \mu\text{m}$) surface with the root mean square surface roughness $< 1\ \text{nm}$. (c) Photo of the evanescent light coupling into the silicon microsphere resonator using a tapered silica optical fiber. The diameter of the silicon resonator is $60\ \mu\text{m}$ and the diameter of the coupling fiber is $2\ \mu\text{m}$. (d) Normalized resonance spectrum of a silicon microsphere with a diameter of $60\ \mu\text{m}$. (e) Normalized resonance dip spectrum of such a silicon resonator at $1563.34\ \text{nm}$.

Limitations of the Q factors are found to be the material loss and the surface roughness of the resonator[153]. To investigate these two factors in our resonator, we characterize both the surface roughness and the crystal structure of the silicon sphere. As shown in Figure 3-13 b inset, an atomic force microscope (AFM) is used to map the surface roughness of the Si sphere. Measurement shows that the root-mean-square (RMS) roughness is $< 1\ \text{nm}$. This ultra-low roughness value indicates that the surface

quality of our resonators is much higher than the resonators fabricated through traditional SOI approaches whose RMS values are typically on the order of a few nanometers. Next, the crystal structure of our fabricated Si spheres is characterized by X-Ray Diffraction (XRD). As shown in Figure 3-13 b, the XRD results confirm its crystalline nature after laser treatment. The crystalline Si sphere resonator offers less absorption loss value than that of the amorphous Si (a-Si)[110]. Note, as shown in Figure 3-8, our approach can produce a batch of sphere resonators with the same diameter in an ordered manner, which makes the resonator fabrication much repeatable and furthermore provides an efficient solution to fabricate resonator arrays (Figure 3-13a). We also investigate the characteristics (surface roughness and XRD) of Bi₂Te₃ and Se spheres fabricated by our method. They both present similar excellent surface roughness and a crystalline structure (see Figure 3-10 and Figure 3-11 for details).

3.6 Summary of Chapter 3

The realization of in-fiber spherical particles centers on the fluid-dynamical behavior of the interaction between different materials in the context of fiber thermal drawing and the following heating process powered by the laser. This is a new playing field for fluid dynamics, with geometries and other parameters that are not accessible in traditional platforms. Further improvements can be realized by the optimization of fiber drawing such as controlling the drawing stress to achieve a more uniform fiber core, which will lead to a smaller variation of the resulting sphere sizes. As opposed to chemical synthesis, this fabrication method highly depends on a physical breakup mechanism. It will not only yield new fundamental insights into fluid dynamics, but also substantially impacts on future developments of photonic, electric, thermoelectric devices, and other related fields

Chapter 4 In-Fiber Material Engineering Based on Laser Recrystallization

4.1 Introduction

During our experiment for fabricating the in-fiber multimaterial spherical particles using the method described in chapter 3, we noticed that the optical properties and dissolution rates of fiber materials had changed after laser scanning, which could be a result linking to fiber material's optical property's being modified during our experiment. This inspires us to develop another in fiber materials engineering method based on the interesting phenomenon. Many studies and literature suggest that these changes should be due to a recrystallization process of core and cladding material after the laser heating. As introduced in chapter 2, multimaterial fiber with a fiber core of single crystal could be achieved through a laser recrystallization process. This technology has been applied in many optoelectronic fibers [10, 109, 110, 117] to generate single crystal multimaterial optical fibers for lowering the optical transmission loss. This approach establishes a stable and precisely controlled melt zone on the fiber across the entire core, leading the fiber core materials to recrystallize during the solidifying. In fact, the generation of single crystal multimaterial fiber is a generic approach, which is not limited to be performed on optoelectronics fiber, but also suitable to fibers for other applications, such as energy harvesting applications which also need single crystal fiber core as the functional part. Towards the purpose of developing high-efficient energy harvesting fibers, we comprehensively investigate the laser recrystallization process for its applications on engineering the thermoelectric material in a fiber.

Tin selenide (SnSe) single crystal, is a novel thermoelectric material that is able to interconvert heat and electricity for power generation or refrigeration. SnSe has attracted much attention in recent years due to its record thermoelectric figure of merit (ZT value) of 2.8 at 773 Kelvin, making SnSe one of the most ideal materials for

thermal energy harvesting applications [108, 155, 156]. Nevertheless, the difficulties in the large-scale synthesis of this single crystal limit its practical applications. What's more, the attributes of rigidity and heaviness of bulky crystals have greatly impeded the increasingly demanded flexible or wearable thermoelectric devices based on SnSe. An important feature of flexible or wearable thermoelectric devices is the capability to cover arbitrary and conformal heat sources to enhance the energy harvesting efficiency and convenience. Here, we fabricate a thermoelectric SnSe fiber by the thermally drawing process mentioned in chapter 2. The resulting thermoelectric fibers are highly flexible, ultralong, and mechanically stable, but in the polycrystalline phase. Furthermore, a laser thermal treatment processing is subsequently employed to melt and recrystallize the SnSe core at a precisely controlled fiber feed-in velocity scanned along the fiber, resulting in a single crystal SnSe thermoelectric fiber. This treatment has dramatically enhanced the fiber's ZT value from 0.58 to 1.94 at 850 Kelvins. The large-scale and low-cost processing approach to producing flexible and high-quality thermoelectric SnSe single crystal fibers will provide a new strategy to develop wearable thermoelectric devices and textiles, which can be seen in our proof-of-concept.

4.2 Functional Fiber Fabrication

To begin the fabrication, a SnSe-core borosilicate-cladding fiber is firstly fabricated by a typical fiber thermal drawing process [8] which is depicted in Figure 4-2a. To fabricate a SnSe-core fiber, a macroscale preform with core-cladding structures was made by loading a SnSe rod into the center of a borosilicate glass tube. To cooperate with the melting temperature T_g and thermal expansion coefficient (TEC) of Tin Selenide, the borosilicate glass tube is used as the cladding material [157-159].

The fiber thermal drawing process includes two steps: (1) preform fabrication and (2) fiber drawing under high temperature. There are three key requirements in the construction of multimaterial fiber preforms[157]. Firstly, the drawing temperature must melt the fiber's core materials. Therefore, the cladding material should be amorphous and its softening temperature (T_g) must overlap the fiber drawing temperature. Furthermore, the fiber drawing temperature cannot exceed the boiling

points of all fiber materials. Lastly, the thermal expansion coefficients (TEC) of all the materials should be comparable, otherwise, the unmatched TECS will induce unwanted thermomechanical forces to generate fractures in the fiber.

According to these constraints, the borosilicate glass is the suitable cladding material for a SnSe core fiber. Firstly, by looking at the information of viscosities (Figure 4-1a), we can conclude that borosilicate glass is able to resist devitrifications which can support SnSe during the thermal drawing process[158, 159]. Secondly, their TECs ($\sim 6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for borosilicate glass and $\sim 3 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ for SnSe) are similar. Herein, a borosilicate glass cladding SnSe core preform is designed and fabricated (Figure 4-1b).

Figure 4-1: **SnSe fiber preform preparation.** (a) Viscosity information of SnSe and borosilicate glass. (b) Schematic of preform preparation.

After making the preform, it is fed into a furnace under a speed of 5 mm per minute. Then the preform is heated in a furnace at 1450 K. When the temperature of the preform is above the melting point T_m of the fiber core material and glass transition

point T_g of fiber cladding material, the preform can be drawn into a smaller diameter fiber at a speed of 0.6 m min^{-1} . The diameter of the fiber core is measured to be $40 \text{ }\mu\text{m}$ and the diameter of fiber cladding is $500 \text{ }\mu\text{m}$. To provide mechanical protection of the fabricated fiber, a $\sim 50 \text{ }\mu\text{m}$ polymer coating layer is coated on the outer surface of the fiber cladding. In addition, by changing the preform feeding speed and the fiber drawing speed, the fiber's total diameter can be further reduced ranging down to 1 millimeter or even sub-nanometers. As the X-ray Diffraction (XRD) results showed in Figure 4-5, the drawn SnSe fiber core is characterized to be polycrystalline at this moment. We note that the thermal drawing process is inducing stress built up due to the difference of LTEC between cladding and core materials and the changed volume contraction in the crystal structure.

Figure 4-2: **Fabrication of SnSe thermoelectric fiber based on fiber thermal drawing process.** (a) Schematic of SnSe fiber preform and thermal drawing process. The drawn SnSe fiber core is characterized to be polycrystalline. (b) Photo of SnSe single-core fiber. (c) Photo of SnSe single core fiber with the yellow polymer coating. The fiber shows great bendability and flexibility. (d) Microscope reflection images of SnSe fiber. The bright white part is SnSe fiber core.

Owing to materials flexibility when they are made into the shape of small-diameter and long-length fiber, the thermoelectric fibers are suitable for flexible

devices. We test the mechanic properties of the fabricated thermoelectric fiber as shown in Figure 4-3.

Figure 4-3: **Mechanical properties of SnSe fiber with different diameters.** (a) Photograph of the fiber redraw process. The SnSe fiber core is redrawn from 500 μm to 125 μm . The fiber feed-in speed is $v_1 = 10 \mu\text{m/s}$ and the fiber drawing speed $v_2 = 160 \mu\text{m/s}$. (b) Microscope image of the 125 μm SnSe fiber. (c) Photograph of the fiber redraw process from 500 μm to 50 μm . The fiber feed-in speed is $v_1 = 10 \mu\text{m/s}$ and the fiber drawing speed $v_2 = 1 \text{ mm/s}$. (d) Microscope image of the 50 μm SnSe fiber. (e) The measured tensile strength versus strain curves of SnSe fibers with different diameters. Young's modulus (E) is also given. (f) The measured bend strength versus deflection (fiber midpoint displacement) curves of SnSe fibers with different diameters. (g) The bend radius of SnSe fiber with a diameter of 125 μm . (h) The bend radius of SnSe fiber with a diameter of 50 μm .

4.3 Laser Recrystallization

4.3.1 Laser Thermal Treatment

For thermoelectric applications, single crystalline SnSe core fiber is desired because single crystallized SnSe shows outstanding properties in extremely high ZT value than a polycrystalline SnSe[108, 156, 160]. Therefore, we develop a laser-induced recrystallization process to alter the polycrystalline SnSe into a single crystal structure. Directional recrystallization of the fibers is undertaken by establishing a stable and limited melt zone across the whole fiber which is similar to the zone-melting single crystal growth method [116]. The translation of the narrow molten region melts the polycrystalline material at its forward edge and leaves a single crystalline material behind it.

Figure 4-4: **Schematic of laser recrystallization treatment on SnSe fiber.** A laser beam with a 500 μm spot size and 2.5 W power provides a stable heating source and the fiber is fed into the laser beam at a controlled fiber feed-in velocity v_f . The laser recrystallization process will transfer the SnSe fiber core from a polycrystal structure into a single crystal structure in $Fm\bar{3}m$ (225) group space. The SnSe single crystal structure is shown as the inset image.

In this study, the continuous wave CO₂ laser as the heating source is used. The laser is at the wavelength of 10600 nm and is strongly absorbed by the borosilicate glass cladding. Thus, the SnSe core melts via conductive heating. The laser focused on the fiber with a beam spot size of 500 μm . The power of the CO₂ laser can be adjusted

from 2.5 W to 18 W. The fiber is feed into the laser spot with a controlled velocity v_f which can be set from 50 to 1000 $\mu\text{m s}^{-1}$.

4.3.2 Single Crystal Formation

Previous studies have suggested that the in-fiber laser recrystallization is controlled by three factors: the heating temperature, the spatial temperature gradient $\frac{\partial T}{\partial z}$ at the solid-liquid interface, as well as the solidification velocity[116, 161]. By changing the output power of the laser together with the fiber feed-in velocity, combinations of these factors can be achieved on this system. In addition, the built-in stress over the core material is also playing a significant positive role in the SnSe core's recrystallization. In fact, the smooth core-cladding cylinder interface, small core diameters, and the limited small molten volume with considerable built-in stress give a chance to increase the growth rate of SnSe single crystal.

In the CO₂ laser thermal heating system, the movement of the solid-liquid interface could be modified by the laser heating temperature and the fiber feed-in velocity. When the laser radiation source is providing a suitable heating temperature to melt the material, the fiber feed-in velocity becomes the key factor in controlling the growth rate. At a high fiber feed-in velocity, a larger temperature gradient ($\frac{\partial T}{\partial z}$) suppresses the nucleation rate and stabilizes the solid-liquid phase interface. The chances of forming the stable nucleus and the time of nucleus growth are reduced. The fiber feed-in velocity cannot be too high to maintain the critical growth rate of a single crystal. Generally speaking, the spreading of the single crystal interface needs sufficient duration. In our experiment, fibers processed at 500 $\mu\text{m s}^{-1}$ and 1000 $\mu\text{m s}^{-1}$ were characterized to generate polycrystalline SnSe core, which proves our hypothesis (Figure 4-5).

On the other hand, if the fiber's feed-in velocity is set to be lower than a certain value, in-fiber capillary instability will be introduced, which is the phenomenon observed in our previous study. This instability will perturb the molten fiber core and restrain the growth of the single crystal. Furthermore, an overly slow fiber feed-in velocity will lead to the formation of multiple crystal nucleus in the core, resulting in

generating polycrystal structures as well. As shown in our experiment (Figure 4-5), a fiber processed at $50 \mu\text{m s}^{-1}$ was characterized to consist of polycrystalline multiple grains. In a short conclusion, a suitable laser heating scanning velocity is the most critical factor for single crystal growth.

Figure 4-5: **XRD spectrum of the crystalline structures of SnSe fiber core generated on different fiber feed in velocity.**

4.3.3 Single Crystal Structure Characterization Based on Electron and X-ray Analysis

To verify our fabrication results, we characterize the recrystallized fiber in detail using different tools, including X-ray diffraction (XRD), Electron Backscatter Diffraction (EBSD), Energy-dispersive x-ray measurement (EDS) and Transmission Electron Microscopy (TEM).

X-ray diffraction (XRD) analysis: The X-ray diffraction measurements were implemented using Nanoinxider Xenocs at the FACTS of Nanyang Technological University. A micro-focus sealed tube-Cu 30 W/ $30 \mu\text{m}$ source is used. The XRD machine with ultra-small resolution ($200 \mu\text{m}$) was used. All SnSe microwires were etched out from the cladding. The XRD machine consists of a Genix 3D X-ray source, 2 sets of scatterless pinholes, a rotatable sample holder with the XY translation stage,

and a detector. X-ray diffraction patterns were measured by two steps: 1) as a function of angle ϕ for rotations at the selected axial positions; 2) as a function of the fiber axial direction (Figure 4-6).

Figure 4-6: **Transmission X-ray diffraction of SnSe fiber core.** (a)Transmission X-Ray Diffraction setup. (b) Schematic drawing of the axial XRD scans of the recrystallized SnSe microwire. (c-f) The X-ray diffraction patterns along laser recrystallized SnSe fiber core at the different axial positions. The white circles highlight the Bragg peak. All patterns are obtained with the same sample orientation angle ϕ , and the diffraction peaks disappeared, and other peaks appeared by changing the orientation angle ϕ . The bright green diffraction rings observed in c-f are due to the polymer scotch tape used as the sample holder.

Following the rotating crystal method[162], we measured the diffraction patterns of the SnSe microfiber at a selected axial position with 30° steps in ϕ . The

patterns were summed up to obtain a rotational diffraction pattern as well as the integrated XRD spectrum. The XRD spectrum of the selected axial position clearly indicates the crystal structure of the SnSe fiber at the selected point.

Figure 4-7: Transmission X-ray diffraction patterns of SnSe powder, as-drawn fiber and single crystal fiber after laser recrystallization. (a) Transmission X-ray diffraction pattern of SnSe powder. The pattern with diffraction rings shows the nature of randomly oriented of SnSe powder. (b) Transmission X-ray diffraction pattern of the as-drawn SnSe fiber core. The pattern with several diffraction peaks shows the nature of the polycrystal structure. (c) Transmission X-ray diffraction pattern of the SnSe fiber core after laser recrystallization. The pattern with a single diffraction peak shows the nature of a single crystal structure.

Furthermore, to analysis the continuity of the crystal structure, we measured the XRD patterns with angle rotations along with the SnSe microfiber per 2 mm. With the ultra-small XRD beam size of 200 μm , the resolution is sufficient to observe the crystalline of the SnSe fiber with a diameter of 50 μm . The serial diffraction patterns obtained exhibit the same peak position, revealing the longitudinal uniformity and stability of the SnSe single crystal structure.

As the nucleating crystallite is likely to be random, different fibers should exhibit different crystal orientations. However, the XRD spectrums indicate that the single crystal SnSe fibers after laser recrystallization have a preferred crystal orientation. The guidance of fiber geometry and the stability in controlled growth rate could be possible reasons. For the liquid-solid single growth method based on the no-seed situation, the existence of preferred orientation at a constant growth rate is well documented.

The XRD spectrum of SnSe powder before drawing is measured by XRD Bruker D8 advance powder machine. Making a comparison of the XRD spectra of SnSe powder to as-drawn fiber, laser recrystallization technology that leads the SnSe from polycrystalline powder to transform into a single crystalline microfiber is well verified. Furthermore, the XRD spectra are taken at 2 mm intervals along with the SnSe fiber core (Figure 4-8). These analyses prove the existence of a long last single crystal of SnSe core fiber with almost permanent orientation.

Figure 4-8: **XRD measurement of SnSe.** (a) XRD spectra of SnSe powder, consolidated rod, fiber core before and after laser recrystallization, indexed according to ICDD PDF-4+ entry no. 00-048-1224 (Pnma (62)), no. 01-084-4082 (Cmcm (63)), and no. 04-003-2929 (Fm $\bar{3}$ m (225)). XRD spectrum of SnSe powder indicates that the SnSe powder is a polycrystal structure in Pnma (62) space group. XRD spectra of SnSe rod and as-drawn fiber indicate that the rod and as-drawn fiber are in polycrystal structure in Pnma (62) and Cmcm (63) space groups. And XRD spectrum of SnSe fiber after laser recrystallization process is a single crystal structure in Fm $\bar{3}$ m (225) group space. (b) XRD spectra of SnSe fiber at 2 mm intervals along the entire laser scanned fiber length.

Electron backscatter diffraction (EBSD) analysis: The XRD characterization also indicates the possible existence of $Fm\bar{3}m$ cubic rock-salt phase. To confirm the structure's creating in the sample, we examine the microstructures of our sample by EBSD. To prepare the sample for EBSD scanning, a SnSe micro-rod was etched out from the borosilicate glass cladding and polished by a focused ion beam (FIB). The EBSD analyses are implemented using HELOS Nanolab 600i with an acceleration voltage of 20.00 kV. The scanning frequency was set at 74.22 Hz.

The EBSD results provide direct experimental evidence that the recrystallized single crystal SnSe structure is in $Fm\bar{3}m$ cubic rock-salt phase. TEM images and selected electron diffraction (SAED) pattern of the structure (Figure 4-11) also support the same conclusion.

Figure 4-9: **EBSD crystallographic map of the as-drawn fiber and after-laser-recrystallization fiber.** (a) EBSD crystallographic map of the as-drawn fiber, with the variation color indicating a polycrystalline orientation. (b) EBSD crystallographic map of the SnSe fiber after the laser crystallization process.

Actually, rock-salt SnSe has been reported to exist as a metastable phase under high pressure in a few early works [163, 164]. As mentioned in the last section, the thermally drawing process and CO_2 laser recrystallization process of silica cladding SnSe core fiber could induce gigapascal-level compressive stress. For the determination of the stress, we investigated the Raman spectra of the SnSe fiber with and without the borosilicate glass cladding to determine the existing of any residual built-in stress. Raman shift data allows of the estimation of stress effects because it causes the intensities and the Raman peak positions of vibrational modes to change corresponding to the stress induced [165, 166]. For SnSe, there are five detected vibrational modes of Raman Spectra that are used for analysis. Based on the variation

of the vibrational modes, we can estimate the stress induced by the fiber thermal drawing process. As shown in Figure 4-10, the black line in the image is the Raman spectrum of SnSe fiber with cladding (with stress). The borosilicate cladding induces a higher baseline to the Raman spectrum. And the red line is the Raman spectrum of SnSe fiber released from cladding (stress released) by HF. By comparing these results with previous studies of pressure-induced SnSe Raman spectra [166], we speculate that the built-in stress is around 7 GPa.

Figure 4-10: **Raman spectra of SnSe fiber with and without borosilicate glass cladding.** Raman spectra were taken at SnSe fiber with cladding and without cladding. The black line in the image is the Raman spectrum of SnSe fiber with cladding (with stress). The borosilicate cladding induces a higher baseline. And the red line is the Raman spectrum of SnSe fiber without cladding (stress released).

Transmission Electron Microscopy (TEM) Analysis: For a better understanding of the crystalline structure inside the fabricated fiber, transmission electron microscopy (TEM) images are taken to observe the details in the microstructure. We prepared the samples for TEM analysis using the focused ion beam (FIB, the HELOS Nanolab 600i). The TEM analyses were implemented using the Tecnai G2 F20 field emission TEM with an acceleration voltage of 200 kV.

Figure 4-11: **TEM observations of a single crystal SnSe fiber core after laser recrystallization.** (a) TEM image of SnSe fiber core in single crystal structure. Top insert, the line profile along AB presenting a spacing is 0.22 nm. (b) Corresponding diffraction pattern.

The images shown in Figure 4-11 demonstrate the single-crystal SnSe phase within the fiber core after the laser recrystallization process. The diffraction pattern is consistent with the crystal SnSe structure in $Fm\bar{3}m$ cubic rock-salt phase, which is also suggested by the EBSD results and XRD results mentioned in the last section. All the evidence provided by XRD spectrum and TEM images suggests the SnSe core is in the single crystal structure with $Fm\bar{3}m$ cubic rock-salt phase.

Energy-dispersive x-ray spectroscopy (EDS) Analysis: Meanwhile, according to the analysis using Energy-dispersive X-ray spectroscopy (EDS) analysis, the laser recrystallization approach does not induce oxidation to the fiber core, which means the rapid degradation of SnSe in the presence of oxygen can be avoided (Figure 4-13).

Based on all characterization results, the conclusion can be drawn that a flexible SnSe/Borosilicate glass fiber is fabricated, and its original polycrystalline core has been transferred into single crystal structure over the scanned region. This single crystal structure is believed to benefit the SnSe fiber's thermoelectric applications. In the next section, we will test the thermoelectric performance of the fabricated single crystal SnSe fiber.

Figure 4-12: **Energy-dispersive x-ray measurement of element distribution in the cross-section of SnSe Fiber.** (a) SEM image of SnSe fiber cross-section. (b) Magnifying SEM images of the SnSe fiber core. (c-f) Energy-dispersive x-ray measurements of Sn, Se, Si and O distribution.

Figure 4-13: **SnSe atomic ratio measured with EDS analysis of SnSe fiber core.**

4.4 Thermoelectric Properties of The Generated Single Crystal SnSe Fiber

Time-domain thermoreflectance (TDTR) method is used to measure the thermal conductivities of the samples involved in this single crystal SnSe fiber. TDTR method is a reliable and well-accepted measurement technique for characterizing thermal properties of nanoscale systems. When it comes to the high-temperature condition, TDTR method is one of few options for researchers. Our two-color TDTR system is similar to the previously reported systems which are modified from the one developed by Cahill [167].

During the measurement, a pulsed Ti:sapphire laser (Spectra Physics, Mai Tai, 800 nm, 100 fs) was used to heat the molybdenum surface of the sample. And at the same time, TDTR system monitors the temperature decay by thermoreflectance with a picosecond resolution by adjusting the optical path difference. Figure 4-14 shows the schematic of TDTR system used in this work. The 1/e² diameters of pump and probe laser spots are 41 μm and 9 μm , focused by a 10 $\times$ objective lens (Edmund Optics, 10X EOM Plan Apo). A CCD camera (Thorlabs, DCC1545M) is used to image the sample. The sample can be found in the nest and the high-quality areas on the sample surface are chosen for TDTR measurement. The wavelength of the pump laser is tuned to 400 nm through BIBO frequency double to achieve the two-color optical design, which could enhance the S/N ratio of the system [168, 169]. The pump pulses are modulated at 3 MHz with an electro-optic modulator (EOM).

Recent studies on thermoelectric properties of SnSe single crystals are mostly based on bulk materials with Pnma and Cmcm phases. The thermoelectric property of a single crystal SnSe fiber with rock-salt $\text{Fm}\bar{3}\text{m}$ phase has not been comprehensively studied so far through the theoretical studies. Moreover, several studies on polycrystalline SnSe bulk materials with rock-salt phase have indicated that rock-salt SnSe is a promising thermoelectric material [170, 171] Figure 4-15 shows the measured Seebeck coefficient, electrical conductivity, thermal conductivity and dimensionless figure of merit ZT along the axial direction as a function of temperature for SnSe fibers with polycrystalline and single crystalline rock-salt structures as comparison. As shown

in Figure 4-15a, both the Seebeck coefficients of polycrystalline and single crystalline SnSe fiber are positive, indicating they are p-type semiconductors. These coefficients demonstrate an increasing trend firstly and then decrease with a maximum of approximately 464 K due to the bipolar effect of minority carrier excitation[170]. The Seebeck coefficient of single crystalline SnSe is measured to be lower than that of polycrystalline SnSe at the same measured temperature, which can attribute to the increased carrier concentration derived from a small energy gap around 0.20 eV and a large electronic density of states in the cubic rock-salt phase[171].

Figure 4-14: The schematic of TDTR system used in this work.

The electrical conductivities of polycrystalline and single crystalline rock-salt SnSe show different temperature-dependent trends (Figure 4-15b). For polycrystalline SnSe fiber, the electrical conductivity is increasing with the increased temperature, and similar with those previously reported in the bulk polycrystalline SnSe, but lower than that of single crystalline rock-salt SnSe at the same measured temperature, which can be explained that the rock-salt $Fm\bar{3}m$ phases lead to high electrical conductivity[171]. While in the single crystalline rock-salt SnSe fibers, the electrical conductivities exhibit metallic transport behaviour from 300 to 464 K and then a change to thermally activated semiconducting behaviour up to 862 K owing to thermal excitation of carriers[160, 171], which is comparable to the electrical conductivities of SnSe single crystals with $Cmcm$ phase[108] and higher than those of polycrystalline SnSe with rock-salt phase[171]. The high electrical conductivity of single crystalline rock-salt

SnSe fiber originates from cubic phase $Fm\bar{3}m$ with a relatively high electrical conductivity, single crystals with less electron scattering, and high pressure in SnSe fiber leading to the enhancement of electrical conductivity[172]. In addition, the high pressure in SnSe fiber also causes that the turning points of the Seebeck coefficient and electrical conductivity curves slightly shift to lower the temperature of 464 K as compared with the reported turning points of 500-550 K[172-174]. The temperature dependence of measured thermal conductivities is presented in Figure 4-15c. These thermal conductivity values are very low and decrease with rising temperature due to the intrinsically low thermal conductivity of SnSe.[171] Moreover, the lower thermal conductivity of single crystal SnSe fiber results from the very higher phonon anharmonicity of its chemical bonds in rock-salt phase.[160] According to the $ZT = S^2\sigma T/k$, where S , σ , T and k are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity respectively, we obtained the ZT values of polycrystalline and single crystalline rock-salt SnSe fibers as plotted in Figure 4-15d. After post-laser recrystallization, the ZT value of single crystal SnSe with rock-salt $Fm\bar{3}m$ phase is as high as 1.94 at 862 K, which is far larger than that of polycrystalline SnSe fiber and comparable to the SnSe single crystals with $Cmcm$ phase.

A lock-in amplifier is used to detect the intensity changes of the reflected probe beam. A ~100 nm Mo film is deposited on the top of the samples as a transducer layer, which heat the sample surface by converting the absorbed pump laser energy and monitor the surface temperature due to the reflectivity change with the temperature. The sample is fixed in a vertical high-temperature heating stage. The sample chamber of the heating stage sized $\phi 7\times 4\text{mm}$ is heated by a platinum filament and protected by helium gas. Platinum-rhodium platinum thermocouple is used to measure the temperature in the sample chamber. The lasers reach the sample across a $\phi 20\text{mm}$ high-transmitting optical glass window. The temperature control system controls the temperature of the sample chamber for measuring the thermal conductivities of samples at different temperatures.

Figure 4-15: **Thermoelectric properties of SnSe fibers.** The measured (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity and (d) dimensionless thermoelectric figure of merit ZT along the axial direction as a function of temperature for SnSe fibers with polycrystalline and single crystalline rock-salt structures.

Table 1: Parameters used in the thermal conductivity model to fit TDTR data.

Layer thickness (d)		Thermal conductivity or interfacial thermal conductance (k or G)	Heat capacity (C_p)
Mo transducer layer	Measured by XRR/TDTR	138W/(m • K)	2.58 J/cm ³ •K
Mo/sample interface	-	Fitting parameter	-
sample	Semi-infinite	Fitting parameter	1.50 J/cm ³ •K

To measure the thermal conductivity of samples, their thickness, thermal conductivity, and heat capacity of the transducer layer must be known. The thermal conductivity and heat capacity for Mo are taken from literature values [reference]. The thickness of the Mo transducer layer is measured by XRR and TDTR acoustic echo method. The modeling parameters are summarized in Table 1.

First-principles calculations based on density-functional theory (DFT) implemented in Quantum Espresso have been performed to obtain the electronic and thermal transport properties of rock-salt SnSe. This approach has been widely used to study the transport properties of thermoelectric materials. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional is used for exchange-correlation energy. The plane wave cutoff energy is set to 45 Ry. The optimized lattice parameter is 6.08 Å, which is in good agreement with the experimental value of 5.99 Å.

The electronic band structure of rock-salt SnSe is shown in Figure 4-16a. The band gap is very small, and it is well known that GGA usually underestimates the band gaps. Since the dispersion of the band structure plays an important role in the electronic transport properties, we do not look forward to the underestimation of the band gap to affect the electronic transport properties significantly. There are three band valleys below the valence band maximum and two band valleys above the conduction band minimum. The deviation of band valleys from high symmetry points results in a larger valley degeneracy number and enhances the thermoelectric power factor.

The electronic transport properties are calculated by employing BoltzTraP package using the semi-classical Boltzmann transport method under the constant relaxation time approximation. A $1 \times 2 \times 2$ supercells of rock-salt SnSe having 32 atoms with a 14 Å vacuum added in the two transverse directions is used to simulate the undoped SnSe fiber. The calculated electronic transport properties in Figure 4-16b are close to the experimental results.

The phonon dispersion along high symmetry lines, as shown in Figure 4-16c, is calculated using Phonopy code. The phonon dispersion of rock-salt SnSe is like that of rock-salt PbTe and SnTe. The acoustic modes converge to 0 at Γ point, showing evidence of thermodynamic stability. Non-analytical corrections are applied to account

for long-range electrostatic interactions based on the Born effective charges and dielectric constants calculated by Quantum Espresso, resulting in the splitting of longitudinal and transverse optical (LO-TO) modes. The overlap between acoustic and optical modes is large due to the small atomic mass difference between Sn and Se. The low-frequency acoustic phonons couple to optical phonons and have high chances to be scattered, leading to a short phonon lifetime and a low thermal conductivity.

Figure 4-16: **Theoretical calculated thermoelectric properties of SnSe fibers.** Calculated (a) electronic band structure, (b) Seebeck coefficient and electrical conductivity, (c) phonon dispersion, and (d) lattice thermal conductivity and figure of merit ZT as a function of temperature for rock-salt SnSe.

The Boltzmann transport equation for phonons is solved within ShengBTE code to obtain the lattice thermal conductivity of bulk rock-salt SnSe. The second-order interatomic force constants (IFCs) are extracted using the Phonopy code, and the third-order IFCs are calculated by the third-order python code using the real-space supercell method. A $3 \times 3 \times 3$ supercell (216 atoms) with a Monkhorst-Pack k mesh of $3 \times 3 \times 3$ is used. The phonon momenta q mesh of $14 \times 14 \times 14$ are used in phonon calculations.

In the calculations, phonons with mean free paths lower than 10 nm contribute to 91% of the lattice thermal conductivity. Therefore, the calculated lattice thermal conductivity of bulk rock-salt SnSe can be used to estimate that of SnSe fiber considering the diameter of SnSe fiber is much larger than 10 nm. The calculated lattice thermal conductivity in Figure 4-16d matches the experimental results. The calculated highest ZT value in Figure 4-16d is 1.3 at 900 K, which is slightly lower than the experiential value due to the negligence of the influences from defects and high pressure in a practical situation, yet has adequately demonstrated that single crystalline rock-salt SnSe fiber possesses a high thermoelectric performance.

4.5 Application of The Generated Single Crystal SnSe Fiber

The measured tensile strength versus strain curves and bend strength versus deflection of SnSe fibers shows that the fabricated thermoelectric fibers are tough, flexible and lightweight enough to maintain the breathability and to be the cornerstones of advanced flexible devices. The thermoelectric fiber can produce electricity from the human body heat dissipation by the counter-thermoelectric effect, resulting in a thermoelectric generator, as well as the body temperature monitor. To increase the energy conversion efficiency, we also design a multicore thermoelectric fiber. The fabrication of multicore SnSe fiber starts with a macroscopic preform including pre-drawn SnSe fibers, borosilicate glass rods, and tube (Figure 4-17a). In shorts for the fabrication, millimetric SnSe fibers obtained from the first thermally drawn step are cut and arranged inside a borosilicate glass tube with a specific shape that is defined and separated by lots of borosilicate glass rods with different diameters. The assembled multicore preform is then vacuum consolidated and thermally redrawn to yield a microscope long SnSe fiber with multicores. Using this iterative stack-and-draw approach, we can further produce a flexible fiber containing high-density SnSe nanowires array. The cross-sectional SEM images in Figure 4-17b and Figure 4-17c show SnSe fibers with two large and small cores, three triangle-shaped cores and four quadrilateral-shaped cores, which plays important role in resistance reduction and thermoelectric p-n type connections.

Figure 4-17e schematically shows that the one end of serial-connected single crystalline SnSe fiber is affixed on the skin surface and the other end is exposed in the environment. As a proof-of-concept demonstration, we serially connect six SnSe fibers and weave them into a shirt (Figure 4-17f and g). The output voltage is 0 mV if the two ends of the fibers share the same temperature (Figure 4-17f). If we put on the shirt (Figure 4-17g), the output voltage of 30 mV is generated because the temperature difference of ~ 10 K is built from skin temperature (35°C) and environment temperature (25°C). Furthermore, the SnSe fiber cores are hermetically sealed in the flexible, electrical and thermal insulated borosilicate glass claddings which prevent the oxidation and degeneration of thermoelectric materials, thus showing good long-term stability during our test.

4.6 Summary of Chapter 4

In summary, we firstly fabricate an arbitrarily long TE fiber by the thermally drawing process with SnSe semiconductor as the core and borosilicate glass as the cladding. Generated thermoelectric fibers are proven to be with good flexibility but in polycrystalline structure, yet the ZT value is only at 0.58 at 850 kelvins. Subsequently, a laser-induced recrystallization process is adapted to establish a stable and precisely controlled melt zone inside the SnSe fiber, where the heat-zone locates across the entire core and scans the fiber as the fiber moves, yielding a continuously single crystal SnSe fiber core over the entire scanned region. Importantly, both experimental and theoretical demonstrate that the ZT value of single crystal SnSe fiber is much higher than that of polycrystal SnSe fiber, reaching 1.94 at 850 kelvins. This study opens a new way to fabricate flexible thermoelectric materials.

Figure 4-17: **Applications of thermoelectric SnSe fibers.** (a) Schematic of fabricating multicore SnSe fibers. (b-c) Cross-sectional SEM images of multicore fibers with different SnSe core numbers and shapes. (d) Flexible SnSe fibers woven into a large-area fabric. (e-f) Demonstrations of the SnSe fibers in the fabric for converting human body heat to electricity.

Chapter 5 Fundamentals of Laser Thermal Treatment for In-Fiber Fabrication and Material Engineering

5.1 Introduction

In previous chapters, approaches for laser-based in-fiber micro- and nanoscale spherical particle fabrication based on capillary instability and in-fiber material engineering are discussed in detail for the experimental designs, materials preparation, setups, procedures of processing, and characterizations of fabricated multimaterial & multifunctional fibers. We have found a precise and stable way to generate high-quality spheres and single crystal in multimaterial fibers. These novel approaches' potential to be applied in optical, electric and biomedical technologies are clearly illustrated with our proof-of-concept experiments.

What is more interesting is that the laser-based in-fiber thermal treatment could induce a number of phenomena that can also be utilized for in-fiber particles and structures fabrication, as well as material engineering. They are achieved over our ability to carefully control the in-fiber heating temperature and the materials cooling rate after heating. To improve the performance of the as-drawn multimaterial fiber, we use a CO₂ laser to manipulate the thermal treatment which could reheat the fiber functional materials with an ultra-limited melt zone and precisely controlled heating temperature. There are 3 key parameters that significantly affect the CO₂ laser-based in a fiber process, which are the laser heating power, the laser spot size, and the fiber feed-in velocity. In brief, the heating power and the spot size determine how much energy is introduced into the small fiber part per unit time and the feed-in velocity decides how long the fiber is staying in the heat zone. Therefore, the cooperation of these parameters would decide the in-fiber heating temperature and the cooling rate over the fiber materials, determining which phenomenon to be performed for the in-

fiber fabrication method. Differing the combination of in-fiber heating temperatures and cooling rates will induce a series of interesting phenomena:

Figure 5-1: In-fiber material engineering system and application

Figure 5-2: Systematically study of laser heating process induced phenomena based on multimaterial fibers. The boiling temperature (T_B) and molten temperature (T_M) are the high and low temperature limitation for the laser-induced in-fiber thermal treatment. The single crystal velocity (v_c) changes according to different materials.

1. **Built-in Stress:** one common existing phenomenon induced by in-fiber thermal treatment is built-in stress. The volume mismatching during the solidification of glass cladding and semiconductor cores will result in gigapascal-level stress applied over the fiber core materials. The existing of built-in stress in the semiconductor core fiber is almost inevitable.
2. **Material Recrystallization:** the melting and resolidation of fiber core at a relatively low fiber feed-in velocity and heating temperature create the possibility for materials recrystallization. Suitable recrystallization conditions provide the path of transferring materials among amorphous phase, polycrystal phase and single crystal phase.
3. **In-fiber Capillary Instability:** with the increasing of laser heating temperature, the solid fiber core and cladding material will be transferred into the liquid phase. The surface tension at the interface between fiber core and cladding during the laser heating process will lead the in-fiber capillary instability and breakup of the core to occur. The breakup period and development of in-fiber capillary instability is mainly controlled by laser heating temperature and fiber feed-in velocity as well.
4. **Laser Trapping:** if the heating temperature keeps increasing, displacement of in-fiber particles is observed during the laser heating process. The laser beam provides an attractive force to the particles and traps them while moving, like a tweezer.

Figure 5-2 illustrates the comparison of heating temperature and fiber feed-in velocity for different laser-induced in fiber phenomena. Firstly, the built-in stress appears nearly in all conditions. Secondly, a small feed-in velocity leads the capillary instability to play a dominating role in the process that is used to produce micro/nano spheres. As the fiber's feed-in velocity increased, the forming of acicular particles instead of spherical particles is realized by us. Furthermore, by increasing the heating temperature, the movement of in-fiber particles can be observed so that the laser trapping is occurring in this melted fiber. Material engineering for the recrystallization of the fiber core is realized with selected feed-in velocities and moderate heating temperatures. If parameters have been changed, the single crystalline fiber core will return to the polycrystalline structure.

Method to achieve in-fiber functional structures fabrication or material engineering is to utilize these phenomena as a combination in one fiber. To make use of them requires a better understanding of each phenomenon theoretically. In this chapter, we will give a detail description of these fantastic phenomena induced by the CO₂ laser heating system and summarize the general conditions for each of them to occur. Next, a comprehensive analysis of the mechanism under each phenomenon will be conducted. Key factors that dominate laser based in-fiber processes are summarized. Thus, the mechanism of each phenomenon can be explained based on fundamental theories and calculations of these key factors. Lastly, we will discuss their advantages in novel applications.

5.2 CO₂ Laser Heating Induced In-Fiber Phenomena and Their Applications

Laser heating temperature and cooling rate are two key parameters that affect every laser heating induced in-fiber phenomenon. Firstly, the results of different laser heating temperatures are discussed. As introduced in chapter 3 and 4, the in-fiber laser heating temperature could be precisely modified by controlling the laser power, the laser spot size and the fiber feed-in velocity passing through the heat zone. Our results suggest that higher laser power and slower fiber feed-in velocity with a fixed laser spot size would induce higher heating temperature into the processed fiber. Therefore, by selecting suitable fiber feed-in velocities, different laser heating temperatures are achieved which lead to different in-fiber phenomena.

When the laser heating temperature reaches the melting point of one fiber material, the scanning laser spot will induce liquidation-resolidification along the fiber axial, resulting in the laser recrystallization process to be developed on fiber core materials. This recrystallization process is used to develop a method for fabricating single crystal core multimaterial fibers.

Furthermore, when the laser heating temperature keeps increasing, the viscosities of core and cladding materials will keep decreasing, letting surface tension play a significant role in materials interactions at their interface. A small external disturbance will cause perturbations occurring at the interface to reduce the surface

energy, which performs as the in-fiber capillary instability phenomena. As seen in our experiment, this fluid instability will lead the continuous fiber core to breakup into a string of spheres, which is used to develop a technique for fabricating in-fiber multifunctional particles. Besides, if the fiber feed-in velocity keeps increasing, the perturbation wave will not have enough duration to complete the forming of spherical particles. Instead, the continuous cylinder core will breakup into acicular particles.

In addition, if the laser heating temperature keeps increasing, we observed that this laser beam can trap fiber particles fabricated in the previous step. This phenomenon can be explained by large temperature gradient forces and scattering forces. In a short conclusion, the laser heating process could induce laser recrystallization, in-fiber capillary instability, and laser trapping phenomena into the multimaterial fibers by controlling laser heating temperature.

Secondly, the cooling rates after laser heating are contributing to several interesting in-fiber phenomena as well. Cooling rates are the temperature variations according to time $\partial T/\partial t$, which is a key factor to decide the likelihood of undercooling at the solidification front during the laser heating process. Our experiment results show that the cooling rate will induce large built-in stress onto the fiber core due to thermal expansion coefficient mismatch between cladding/core materials and volume contraction changing in crystal structures. According to previous studies, gigapascal-level built-in stress could be induced onto the fiber core making of semiconductors material. This large built-in stress provides the possibility to modify the material electronic bandgap as well as to influence the recrystallization process mentioned above.

Based on the combinations of laser heating temperature and cooling rate, in-fiber built-in stress, materials recrystallization, capillary instability and laser trapping are achieved respectively. Here, We discuss these phenomena and their applications in detail.

5.2.1 In-Fiber Built-In Stress

5.2.1.1 Formation of the in-fiber built-in stress

As mentioned in previous chapters, every thermal treatment process in a multimaterial fiber, including thermal drawing process and laser heating process, will induce large built-in stress onto the fiber cores. This effect becomes much significant when the fiber core is made with semiconductor materials.

A possible mechanism that could explain the formation of built-in stress is the residual stress resulting from the mismatching of linear thermal expansion coefficients (LTEC) between fiber cladding and core materials. Meanwhile, the laser heating process will let recrystallization of core material happen simultaneously, which may change the volume of the fiber core, while the volume of fiber cladding material keeps constant. The mismatch of the fiber core and cladding's volume would result in built-in stress occurring on the fiber core as well. Since the mismatches in volumes are due to the intrinsic properties of fiber materials, this kind of stress cannot be completely avoided based on known approaches.

Previous studies have spent many efforts on reducing the built-in stress because this gigapascal-level stress in the inner surface of the cladding would create cracks on fiber. Therefore, the stress is an unstable factor and hidden trouble for maintaining fiber's mechanical properties.

Instead of seeing the built-in stress as a negative result from the in-fiber laser processing, to utilize the stress for materials engineering is considered by us for the interest to fabricate semiconductor particles. Creating stress between two semiconductor particles has been proven to be useful in tuning the electronic bandgap of the two-particles semiconductor device, which would be of great significance in photonic and optoelectronic application [175-177]. Therefore, the ability to generate tunable bandgap semiconductor particles with controlled stress over their interface could pave a route toward advanced in-fiber integrated electronic and optoelectronic multifunctional devices.

5.2.1.2 Application of in-fiber built-in stress: material electronic banding modification

Here, we describe the method for introducing stress in-fiber based on laser heating process and applied this phenomenon into material electronic banding modification.

The existing of built-in stress during the laser heating process was shown with cracks observed in thin-cladding fibers. Some semiconductor materials, such as Si, Ge, and GaSb, expand up in solidification. However, because the solidification temperatures of Si, Ge and GaSb are lower than the softer temperature of silica, they are blocked to their liquid volume when reaching the solidification temperature by the surrounding silica cladding. The expanding during spherical particle formation causes the spheres to strain the surrounding silica cladding and to induce internal built-in stress.

Figure 5-3: 130 μm silicon spherical particles and stress patterns around silicon spherical particles observed in the microscope with cross-polarizers. (a) In-fiber silicon micron spherical particles fabricated by laser-induced capillary instability. The laser power is 7 W, and the fiber feed-in velocity is $10 \mu\text{m s}^{-1}$. The laser spot size changes from 2 mm, 1.5 mm, 1 mm to 0.5 mm resulting in a changing cooling rate. (b) Stress evaluation in the cladding of the sphere through the birefringence measurement. Intensity distribution for samples fabricated by different laser spot sizes, as is observed through a transmission optical microscope in crossed polarizer configuration. The number of fringes N increase from 1 to 2 with the increasing of stress.

In our study, the resulting stress is quantified through photoelastic measurement. Indeed, the built-in stress in spheres presents as strain in silica cladding, alters the refractive index of silica. Therefore, the birefringence pattern can be seen under light illumination. As shown in Figure 5-3a, the silicon-in-silica micron spheres are fabricated using a CO_2 laser under a controlled fiber feed-in velocity ($10 \mu\text{m s}^{-1}$). To control variables, we modified the laser power and spot size to maintain the highest

temperature around 2000 K. By changing the spot size (0.5, 1, 1.5 and 2 mm), the solidification process could be precisely controlled, resulting in the precise modification of built-in stress.

Firstly, birefringence patterns with multiple Michel-Levi rings around the spheres (Figure 5-3b) are observed [178]. This pattern enables us a way to estimate the level of the built-in stress qualitatively by the number of Michel-Levi rings. From the results showing in Figure 5-3b, we can conclude that the number of Michel-Levi rings increases from 1 to 2, which means the built-in stress keeps increasing when we reduce the laser spot size.

Another technique we use to quantify the in-fiber stress is Raman spectroscopy with a 532 nm wavelength laser. For silicon under stress, the position ω first order Raman peak depends on the pressure P according to $d\omega/dP = 5.2 \pm 0.3 \text{ cm}^{-1} \text{ GPa}^{-1}$ [179]. As shown in Figure 5-4, the Raman peak shifts on the silicon spheres fabricated with laser spot sizes of 2 mm, 1.5mm, 1mm and 0.5 mm are 4.25 cm^{-1} , 4.67 cm^{-1} , 5.82 cm^{-1} , and 8.38 cm^{-1} compared with a silicon wafer. These shifts can be translated to be corresponding to stresses of $0.82 \pm 0.05 \text{ GPa}$, $0.90 \pm 0.05 \text{ GPa}$, $1.12 \pm 0.06 \text{ GPa}$, and $1.62 \pm 0.09 \text{ GPa}$. Next, we released these spheres from the silica cladding and measured their Raman spectra again. Comparing with a silicon single crystal wafer, the first order Raman peak of these silicon spheres is locating at $\sim 518 \text{ cm}^{-1}$ associated with the polycrystal structure. In conclusion, the Raman peak shift between the spheres with and without cladding indicates the large built-in stress's existence on the silica/silicon interface.

The gigapascal-level built-in stress in the core materials will change the material lattice spacings, and the radius of the Debye cone, thus tailoring the electronics and optics properties of functional materials. Therefore, the ability to control the built-in stress on in-fiber functional materials paths us a new route to modify the material crystal lattice, as well as the electronics bandgap for special application and fabrication of in-fiber stressed-structures.

Figure 5-4: **Raman shift comparison between the released silicon spherical particles and the particles in the fiber cladding.** (a) Raman shift of silicon spheres without cladding and a silicon wafer as a reference. The silicon wafer indicates the Raman peak of single crystal structure silicon without stress or strain. The Raman peaks of silicon spheres indicate their polycrystal structure without any stress or strain. The inset is the microscope image of 130 μm released silicon spheres. (b) Raman shift of silicon spheres in cladding with different stress. Compared with the reference Raman peak of the silicon wafer, the Raman peaks shift to the right with the increasing laser spot size, which related to the increased cooling rate and increasing built-in stress.

5.2.2 CO₂ laser Induced In-Fiber Material Recrystallization

5.2.2.1 Mechanism of laser induce material recrystallization

As noticed in previous experiments a relatively lower laser heating temperature cannot induce capillary instability into the fiber core even if the fiber core has been

melted due to the relatively large viscosity ratio and perturbation develop duration. However, we have also found that the cladding and core materials perform different dissolution rates and refractive indexes after the laser heating process as compared to its original measurement. Several kinds of literature have mentioned that the possible explanation of fiber materials' optical properties and dissolution rates before and after the laser heating process can be summarized to be the changing of material's crystal structures.

The smooth core-cladding cylinder interface, small core diameters, and the limited small molten volume with considerable built-in stress give a chance to fabricate single crystal fiber[119, 120]. Laser heating process with suitable laser power and a fixed spot size creates a narrow melting zone on fiber material which could be scanned across the fiber under selected velocity, performing as an in-fiber zone-melting recrystallization process on the fiber's functional core materials. Furthermore, the large built-in stress introduced on the fiber core is another preferable condition for crystal growth, which will influence the crystal growth rates and determine the phase of the achieved single crystal structure as well.

The recrystallization process is controlled by three factors: the heating temperature, the spatial temperature gradient at the solid-liquid interface, as well as the solidification velocity[116, 161]. The main purpose of the laser recrystallization system is to provide a stable nucleation rate and sufficient duration for the single crystal interface development. When the laser radiation source is providing sufficient energy for melting the material, the fiber feed-in velocity becomes the key factor for the crystal's growth rate. If the fiber feed-in velocity is higher than the single crystal critical growth rate, the larger temperature gradient will suppress the nucleation rate and reduce the time of nucleus growth resulting in forming a polycrystal structure. On the other hand, if the fiber feed-in velocity is overly slow, it creates conditions for growing multiple grains which will develop into polycrystal structure. Also, the relatively slower fiber feed-in velocity could induce in-fiber capillary instability to totally destroy any formed single crystal structure and stop the crystallization process.

Hence, a suitable temperature gradient and fiber feed-in velocity could also suggest a suitable single crystal growth rate under the laser recrystallization process.

To investigate the heating and melting dynamics in the laser recrystallization process, a simulation model is developed based on a cylindrical SnSe-Borosilicate glass fiber system.

A widely used method to estimate the temperature distribution in one fiber is to measure the emission intensity profiles and the blackbody with emissivity parameters of materials. However, the emissivity parameters of plenty of materials need to be tested. For example, there is no suitable value from literature for the emissivity parameter of SnSe. Therefore, we develop a three-dimensional axisymmetric numerical finite element method simulation by the software COMSOL for modeling of CO₂ laser-induced heat transfer in fiber. A general heat transfer equation has created a base on the general energy balance

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla T = \nabla \cdot (k \nabla T) + Q \quad \text{Eq. 2}$$

where ρ is the local density of the materials; C_p is the specific heat capacity; T is the local temperature; u is the fluid velocity of materials, and Q is the heating power per unit volume[180]. Coupled with the Navier-Stokes equation, the heat transfer equations are solved by using the Heat Transfer Module in COMSOL. We develop a 3D heat transfer model that simulates the process of a CO₂ laser heating source moving along a SnSe core borosilicate glass cladding fiber. By changing the parameters, the model indicates that the heating temperature in the fiber is a function of fiber feed-in velocity and laser heating power. Furthermore, we could figure out the temperature variations according to time $\frac{\partial T}{\partial t}$ (cooling rate) or along the fiber $\frac{\partial T}{\partial z}$ (temperature gradient) from the temperature profiles calculated by the model.

The simulation model could describe a thermal profile along the fiber during the laser heating treatment. Furthermore, this model also allows the estimating of the thermal gradient of the solidification front as a function of heating power and fiber feed-in speed. At a suitable laser heating temperature, increasing of the fiber feed-in velocity leads to a larger thermal gradient. For example, when the laser scans the fiber at 2.5 w with 100 $\mu\text{m s}^{-1}$ fiber feed-in velocity, the temperature of fiber core can reach 1250 K and the thermal gradient is 300 K mm^{-1} . This factor is higher than the typical thermal gradients measured in the bulk crystal material fabrication process but it is

comparable with those measured in laser recrystallization processes [10, 108, 181]. Besides, the emission light of the melt SnSe core recrystallization process was recorded. The emissivity of the melting SnSe core covers the visible-wavelength range. The absorbance and emissivity of the borosilicate glass are low, allowing the recording of the melting and solidification process. Figure 5-5 shows the emission profile during the laser recrystallization process of the fiber at 2.5 W laser power with $100 \mu\text{m s}^{-1}$ fiber feed-in velocity as well the related simulation of the temperature profile.

Figure 5-5: (a) Emission of SnSe and silica during the laser recrystallization process and (b) related simulation of the temperature profile.

5.2.2.2 Application of in-fiber laser recrystallization: Single crystal thermoelectric fiber with high ZT value

As introduced in Chapter 2, the laser-induced recrystallization process has been applied in the fabrication of semiconductor fiber (Si, Ge, SiGe, GaSb) for many photonics and optical applications. In addition, we applied this phenomenon to the fabrication of thermoelectric single crystal SnSe fiber as discussed in Chapter 4. The fabricated single crystalline rock-salt SnSe fibers possess high thermoelectric

properties, dramatically enhancing the ZT value from 0.58 to 1.94 at 862 Kelvin. These large-scale and low-cost processing approaches to produce flexible and high-performance thermoelectric SnSe single crystal fibers will provide a new strategy to develop wearable thermoelectric devices and textiles.

5.2.3 In-fiber Capillary Instability

With the increase of the laser heating temperature, the growth of single crystal will be substituted by another phenomenon, the in-fiber capillary instability.

5.2.3.1 Theory of in-fiber capillary instability

The in-fiber instability phenomenon that we utilized into the particles fabrication process can be well explained by Plateau-Rayleigh linear instability theory, which is also called Rayleigh instability linear theory or PR linear instability theory, theoretically describes the physical phenomenon that a liquid column presents to break-up into small spheres which have the same volume. The conditions for the break-ups to occur are (a) liquid column is surrounded by another kind of material, and (b) the liquid column's length is long enough. We backtrack to the original work of Rayleigh in 1878[133]. Using linear stability analysis, he originated a critical parameter, the critical wavelength scale λ_{crit} , to estimate the development of perturbation.

Figure 5-6: **Plateau-Rayleigh linear instability theory model.**

According to the PR instability theory, the solution for the value of the perturbation growth rate q as a function of core viscosity η_{inner} , cladding viscosity η_{outer} and wavenumber ka .

$$q = \frac{T}{2a\eta_{outer}} (1 - (ka)^2) \Phi(ka, \frac{\eta_{inner}}{\eta_{outer}}), \quad \text{Eq. 3}$$

In Eq. 3, the function Φ is a function of $\mu' = \mu_{inner}$, $\mu = \mu_{outer}$, $I_n(x)$ and $K_n(x)$

$$\Phi(x) = N(x)/D(x), \quad \text{Eq. 4}$$

$$N(x) = I_1(x)\Delta_1 - \{xI_0(x) - I_1(x)\}\Delta_2, \quad \text{Eq. 5}$$

$$D(x) = \left(\frac{\mu'}{\mu}\right)\{xI_0(x) - I_1(x)\}\Delta_1 - \left(\frac{\mu'}{\mu}\right)\{(x^2 + 1)I_1(x) - xI_0(x)\}\Delta_2 \\ - \{xK_0(x) + K_1(x)\}\Delta_3 - \{(x^2 + 1)K_1(x) + xK_0(x)\}\Delta_4 \quad \text{Eq. 6}$$

In the function $D(x)$, Δ_1 , Δ_2 , Δ_3 and Δ_4 are all 3×3 determinants as follows:

$$\Delta_1 = \begin{vmatrix} xI_0(x) - I_1(x) & K_1(x) & -xK_0(x) - K_1(x) \\ I_0(x) + xI_1(x) & -K_0(x) & -K_0(x) + xK_1(x) \\ \left(\frac{\mu'}{\mu}\right)xI_0(x) & K_1(x) & -xK_0(x) \end{vmatrix}, \quad \text{Eq. 7}$$

$$\Delta_2 = \begin{vmatrix} I_1(x) & K_1(x) & -xK_0(x) - K_1(x) \\ I_0(x) & -K_0(x) & -K_0(x) + xK_1(x) \\ \left(\frac{\mu'}{\mu}\right)I_1(x) & K_1(x) & -xK_0(x) \end{vmatrix}, \quad \text{Eq. 8}$$

$$\Delta_3 = \begin{vmatrix} I_1(x) & xI_0(x) - I_1(x) & -xK_0(x) - K_1(x) \\ I_0(x) & I_0(x) + xI_1(x) & -K_0(x) + xK_1(x) \\ \left(\frac{\mu'}{\mu}\right)I_1(x) & \left(\frac{\mu'}{\mu}\right)xI_0(x) & -xK_0(x) \end{vmatrix}, \quad \text{Eq. 9}$$

$$\Delta_4 = \begin{vmatrix} I_1(x) & xI_0(x) - I_1(x) & K_1(x) \\ I_0(x) & I_0(x) + xI_1(x) & -K_0(x) \\ \left(\frac{\mu'}{\mu}\right)I_1(x) & \left(\frac{\mu'}{\mu}\right)xI_0(x) & K_1(x) \end{vmatrix}, \quad \text{Eq. 10}$$

With the Eq. 4 - Eq. 10, we can plot the growth rate q with the development of wavelength x . The wavelength x ($x=ka$) can be decided when the growth rate q reaches its maximum. With all the equations above, a theoretical system about the perturbation wavelength of capillary instability is established.

The growth rate of perturbation: With the comparison of q , we can develop a mathematics system to predict the phenomenon of capillary instability. The function of q is related to the part of $(1-(x)^2)\Phi(x)$.

$$q = \frac{T}{2a\eta_{outer}}(1 - (x)^2)\Phi(x, \frac{\eta_{inner}}{\eta_{outer}}), \quad \text{Eq. 11}$$

As the example mentioned in Tomotika theory, in the black lubrication oil and golden syrup two-layer fluid system, the $\mu_{inner}/\mu_{outer}=0.91$. Therefore, when $x = 0.568$, q can reach the maximum. And the wavelength of perturbation can be calculated by $\frac{2\pi a}{\lambda} = x_{qmax}$.

Figure 5-7: Curve of $(1-x^2)\Phi(x)$ with $\mu_{inner}/\mu_{outer}=0.91$.

Instability Growth Factor of Isothermal Heating System: When materials of fiber are heated in a uniform temperature environment, the temperature of each part of this fiber will be heated to the same. In this situation, the traditional analysis method of capillary instability can be applied.

By the conclusion of Tomotika theory, we can establish a function between the growth rate and the viscosity ratio. As the viscosity ratio changes with temperature, the growth rate could be expressed by a function based on the temperature. In another word, we could develop a function between the perturbation wavelength and the temperature to describe the in-fiber instability phenomenon. The temperature-based wavelength provides the possibility of controlling the sphere size by changing temperature. In our copper-core and silica-cladding model fiber, A simulation model is built to study the in-fiber capillary instability at the temperature from 1400 °C to 2400 °C, near the boiling point of copper. In this method, the diameter of the sphere fabricated from the capillary instability also could be calculated using the equation below.

$$\frac{D_{sphere}}{D_{core}} = \left(\frac{1.5\lambda}{D_{core}} \right)^{\frac{1}{3}}, \quad \text{Eq. 12}$$

Figure 5-8: Viscosity ratio of copper and silica (solid black line, left axis) and the amplification ratio of wavelength and fiber core diameter (solid blue line, right axis).

However, by comparing the experimental results of our laser-induced capillary instability microsphere fabrication (Figure 3-8), it can be found that the simulation result does not perfectly match with our experiment result. Obviously, the traditional capillary instability models are hard to be applied in a non-uniform heating situation. In our laser-induced in-fiber capillary instability system, the situation is more complicated due to the inhomogeneous of the thermal field. More conditions should be considered to improve the simulation process.

Instability Growth Factor of Laser-Induced Gradient Heating System: As discussed above, the traditional capillary instability theory is not suitable for describing the laser-induced in-fiber capillary instability situation, which is a non-uniform heating process. Although the simulation result based on Tomotika theory shows a similar trend with the experiment result, the errors between the simulation and experiment result cannot be ignored. J. J. Kaufman et al. demonstrated a fiber processing method using a flame as a heat source, the fiber was no longer settled in a uniform and the stable heating environment. Following the discussion of this paper, we can develop the instability growth factor based on some existing theories [136, 147].

The fiber will be fed into a laser beam controlled by the feed-in velocity. The laser beam spot size is around 300 μm which is much shorter than the fiber length. Only the selected part of the fiber of the laser beam will be heated. Considering this process,

the fiber feed-in velocity plays the most significant role because it determines the temperature over the small part of the fiber. Also, a much shorter length of heated fiber also involves more changes for the mathematics calculation. What's more, there is a thermal gradient along the fiber which we cannot be ignored. Therefore, an improved theory based on the Tomotika theory is strongly needed.

In Tomotika theory, every point on the interface of fiber is treated as the same. They are assumed to be in the same status, heated to the same temperature and having identical boundary conditions. There is no doubt that this assumption is no longer applicable in the laser heating situation. The temperature along the fiber is not uniform, presenting a thermal gradient along the fiber. Thus, points along the fiber will be measured with different temperatures to give a different viscosity of material at this point. Hence, the condition with position-dependent temperature setting is considered into the new theory.

From the growth factor of the isothermal heating situation, we can summarize the relationship between the perturbation amplitude ε and the fiber core diameter a

$$\frac{d}{dt} \left(\ln \left(\frac{\varepsilon}{a} \right) \right) = \frac{T(1-x^2)\phi(x)}{2\mu r_{core}}, \quad \text{Eq. 13}$$

In the modified model, the ratio between the sphere diameter and the core diameter is around 3 to 4. Thus, $\ln(\varepsilon/a)$ is around 1 [9], [46]. And the equation above can be developed as

$$\ln \left(\frac{\varepsilon}{a} \right) = 1 = \int_{t_0}^{t_{end}} \frac{T(1-x^2)\phi(x)}{2\mu r_{core}} dt = \frac{T(1-x^2)\phi(x)}{2\mu r_{core}} (t_{end} - t_0) = \frac{T(1-x^2)\phi(x)}{2\mu r_{core}} \Delta t, \quad \text{Eq. 14}$$

where t_0 and t_{end} is the start and end time of perturbation wavelength development. Therefore, the development time Δt which is needed by the perturbation to develop into spheres could be presented by

$$\Delta t = \frac{2\mu r_{core}}{T(1-x^2)\phi(x)} = \frac{1}{q}, \quad \text{Eq. 15}$$

When we consider that the fiber is settled under the laser beam and the fiber is heated with a thermal gradient, we introduce a position-depended temperature and viscosity function into the equation.

$$\ln\left(\frac{\varepsilon}{a}\right) = 1 = \int_{t_0}^{t_{\text{end}}} \frac{T(\lambda, t)(1-x^2)\phi(x)}{2\mu(\lambda, t)r_{\text{core}}} dt, \quad \text{Eq. 16}$$

$$x = v_f t - \lambda, \quad \text{Eq. 17}$$

The function $x(t, v_f)$ is the position of the molten fiber at the time t with the feed-in velocity v_f . The heating temperature and the viscosities both depend on the feed-in velocity v_f . We develop a new perturbation wavelength function based on the feed-in velocity and fiber core diameter. With the new function, we create a new theory to describe the laser-induced in-fiber capillary instability. By calculating the minimal of t_{end} , we could find out the wavelength of perturbation. In the modified simulation model, we examine this method using a copper-core and silica-cladding fiber.

Figure 5-9: **Simulation of the amplification ratio r_{am} as a function of fiber feed-in velocity v_f by laser-induced in-fiber capillary instability.**

The simulation result is shown in Figure 5-9 and the amplification ratios have a linear relationship with the fiber feed-in velocity, which indicates that a slower velocity leads to a shorter wavelength. Furthermore, the simulation results show the same trend and comparable values with the results of our experiments (shown in Figure 3-8). The fine distinctions between them might be from the perturbation growth rate which we used. The perturbation growth rate may differ than the real case and results

in the discrepancy. The theoretical study of laser induced in-fiber capillary instability helps us to understand this phenomenon more deeply and provide a prediction for any other materials.

5.2.3.2 Application of in-fiber capillary instability: in-fiber functional particle fabrication

As the discussion in Chapter 3, the laser induces in-fiber capillary instability can be used to fabricate in-fiber spherical particles with diameters from 200 nm to 250 μm (Figure 5-10a). In addition, this fabrication method is also applicable to the fabrication of in-fiber particles with other shapes, such as acicular particles (as shown in Figure 5-10b). By controlling the heating temperature and fiber feed-in velocity, we can reduce the growth rate of the perturbation wave and make the droplet solidify with the acicular shape. Furthermore, the in-fiber particles with a complex structure (core-shell structure, multilayer structure and hollow structure) can also be achieved by this fabrication approach.

Figure 5-10: **In-fiber nano/micron spherical and acicular particles fabrication based on laser-induced in-fiber capillary instability.**

5.2.4 In-fiber Laser Trapping and Movements of Generated In-Fiber Particles

When the in-fiber heating temperature keeps increasing, the in-fiber particles generated from capillary instability will leave their original positions (fiber core) and

move towards the laser beam position. In other words, these particles are trapped by the laser beam. Observation suggests that the laser is able to keep generated particles at the center of its beam and move them when the beam shifts. Through a literature review, this movement of particles is suggested to be generated by the laser trapping force based on the temperature gradient. This is the observation of in-fiber laser trapping phenomenon for the very first time as far as we know (as shown in **Figure 5-11**).

Figure 5-11: Movement of in-fiber silicon micron spherical particles based on a laser trapping process. The laser beam is focused on the silicon sphere in the center and the sphere is trapping to move up to the cladding surface.

Laser beam induced in-fiber laser trapping phenomenon has great development potential and good application prospects. For example, the in-fiber functional particles could be trapped into a designed arrangement for sensor and resonator application as shown in Figure 5-12a.

Utilization of the in-fiber laser trapping phenomenon creates a new path for producing in-fiber multifunctional PN molecules over two spheres as shown in Figure 5-12b. The in-fiber P-type and N-type spheres pair could be achieved by dual cores fiber. However, it is hard to fabricate this PN spheres junction directly only relying on the in-fiber capillary instability due to the mismatching of breakup periods and repulsive forces during the sphere's formation period. The P-type and N-type spheres pair always present separately as shown in Figure 5-12b (1) with a certain distance. Therefore, the laser trapping process gives us hope to create the contacting of P-type and N-type spheres precisely to form a PN junction in fiber.

Figure 5-12: **In-fiber laser trapping for multimaterial particles for designed structure fabrication.** (a) In-fiber particles with a designed arrangement for sensor and resonator application based on laser trapping. (b) In-fiber PN junction fabrication based on laser trapping.

5.3 Summary of Chapter 5

In this chapter, more laser-induced in-fiber phenomena that could be utilized for in-fiber fabrication and materials engineering are discussed. The CO₂ laser-assisted system developed by us has adjustable parameters including laser's heating power, spot size and fiber's feed-in speed. By selectively setting these parameters, we gain the ability to control two important impact factors in each laser-induced heating process: the in-fiber temperature and the cooling rate. We comprehensively study how these two impact factors affect the laser-induced heating process fundamentally by theoretical modeling and software simulations. The study allows us to make use of the in-fiber built-in stress, the in-fiber material recrystallization, the in-fiber capillary stability and the in-fiber laser trapping for developing methods of fabricating bandgap adjustable sphere semiconductor devices, high-quality TE fiber devices, uniform or asymmetry shaped particles as well as spheres PN junctions. It is worth noting that, there are still plenty of rooms under the utilization of the laser-induced in-fiber processing system for developing more applications. For one thing, exploiting of the current four in-fiber phenomena for producing multimaterial and multifunctional fibers is requesting more studies and innovations towards wider applications. For another thing, investigation on more in-fiber phenomena could path a new way for novel studies. We foresee that

multimaterial fibers with more advanced functions are going to be created from these approaches.

Chapter 6 Summary and Outlook

6.1 Outlook and Future Work

In this thesis, we have discussed the observation of in-fiber laser-induced phenomena and their interesting applications for in-fiber fabrication and material engineering. We have also explored the relevant theories and mechanism from the fundamentals of capillary instability and thermal dynamics. In this section, we will discuss the directions for the future development of this work based on the results presented in this thesis.

6.1.1 In-fiber Gradient-Index Micron Lens Fabrication Based-On the Precisely Controlled Built-In Stress

As discussed in Chapter 5, the laser-heating process could induce gigapascal-level built-in stress into the in-fiber semiconductor particles and we also prove the possibility to control this stress. As the stress is applied by the fiber silica cladding at the outer surface of the core semiconductor materials, it is not homogenously distributed in the spheres. Whereas, the stress decreases from the outer to inner where the material refractive index changes with the applied stress and strain, which enables the creation of in-fiber gradient index (GRIN) semiconductor micron lens. A possible challenge for achieving this application is to study the physical principle of the laser-induced built-in stress and to apply the stressed micron semiconductor sphere into the integrated optical system as a GRIN lens.

6.1.2 In-fiber PN Junction Particle Pairs with More Complex Structure and In-Fiber Integrated Devices

The dual cores of a multimaterial fiber could be transferred into paired particles by the laser-induced capillary instability phenomenon. Then, these paired particles in P-type and N-type could be combined with the laser trapping process. However, there is no way to operate the in-fiber PN junctions without bias potentials that must be

supplied with conductive wires. Furthermore, the in-fiber PN junctions are in a very basic structure now. More complex structures and designs are required for achieving excellent performance optoelectrical fiber devices. The main challenge here is to achieve an integrated fiber system with P-type materials, N-type materials, insulators and conductive wires.

6.2 Summary and discussion

This thesis starts with the analysis of observed laser-induced in-fiber capillary instability and designs a CO₂ laser based in-fiber thermal treatment system for in-fiber fabrication and material engineering. The laser beam introduces a precisely controlled melting zone and thermal gradient, which induce plenty of interesting phenomena and changes into the fiber structure and its materials properties. By changing the laser heating temperature, heating spot size and fiber feed-in velocity, we can achieve well controlling of the heating process to allow single crystal fiber fabrication, in-fiber functional particle fabrication, in-fiber particle relocation by laser trapping and material electronic banding modification to take place respectively. In summary, there are three major contributions of this thesis.

For the first contribution, we develop a precisely controlled and universal in-fiber fabrication approach for in-fiber micron and nanoscale spherical particles based on CO₂ laser-induced in-fiber capillary instability, which can achieve

- A CO₂ laser heating system, which can be applied in metal, semiconductor, chalcogenide glass and functional polymer fibers with melting temperature from 400 K to 2400 K and 10 orders of differences in fiber core/cladding viscosity ratio;
- An in-fiber micro/nano spherical particles fabrication approach with features of highly uniform diameter, an ultra-smooth surface, and crystalline structure;
- Silicon-based whispering-gallery mode resonators fabricated by this approach achieving the Q factor as high as 7.1×10^5 .

For the second contribution, we devise a thermoelectric single crystal SnSe fiber production process based on CO₂ laser-induced in-fiber recrystallization for achieving flexible and wearable thermoelectric fiber with high ZT value, which has features as:

- In-fiber CO₂ laser heating system for SnSe single crystal fiber fabrication in Fm $\bar{3}$ m (225) group space;
- The ZT value was improved from 0.58 to 1.94 at 862 K;
- New fiber structures with multiple fiber cores and variable diameters have been realized to produce high-efficient single crystal energy harvest fiber for large-area fabrics and wearable thermoelectric devices.

For the third contribution, we construct an in-fiber CO₂ laser thermal treatment system for in-fiber integrated structure fabrication and material engineering. We study the following phenomena and their feasible applications:

- In-fiber gigapascal-level built-in stress, laser recrystallization, in-fiber capillary instability and laser trapping.
- Achieving in-fiber single crystal growth and electric bandgap modification, as well as functional particle fabrication with precisely designed structure and distributions.
- Simulation models of the in-fiber laser heating system are also built to investigate the thermodynamic and microfluidics.

Appendix

Appendix 1: Silicon Based WGM Resonators

Si Resonator Structure	Resonator Size	Q factors	Ref
Microdisk	2.5 μm	4.7×10^5	[182]
Microdisk	4.5 μm	3.5×10^5	[183]
Microcylinder	1-2 μm	2.8×10^4	[184]
Microcylinder	1.91 mm	2.1×10^3	[185]
Microsphere	530 μm	2×10^5	[186]
Microsphere	500 μm	1×10^5	[187]
Microsphere	25.4 μm	4×10^5	[154]
Microsphere	2.49 μm	$\sim 1 \times 10^3$	[188]
Microsphere	60 μm	7.1×10^5	Our Result

Publications

Journal:

1. **J. Zhang**, K. Li, T. Zhang, P. J. Buenconsejo, M. Chen, Z. Wang, M. Zhang, Z. Wang, and L. Wei, Laser induced in-fiber fluid dynamical instabilities for precise and scalable fabrication of spherical particles, *Advanced Functional Materials* 27, 1703245 (2017).
2. **J. Zhang**^{1#}, T. Zhang^{1#}, Z. Wang, Z. Chen, C. Li, Z. Wang, K. Li, S. Chen, X. Huang, H. Zhang, Z. Tian, H. Chen, Z. Ren* and Lei Wei*, Laser recrystallized SnSe single crystal fiber with high thermoelectric performance, *Preparing* (2018)
3. T. Zhang, K. Li, **J. Zhang**, M. Chen, Z. Wang, S. Ma, N. Zhang, and L. Wei, High-performance, flexible, and ultralong crystalline thermoelectric fibers, *Nano Energy* 41, 35-42 (2017).
4. Y. He, Z. Wang, **J. Zhang**, and L. Wei, A stable and long-lasting concentration cell based on reduced graphene oxide membrane and natural resource electrolyte, *Journal of Materials Chemistry A* 5, 21130-21133 (2017).
5. D. Cui, X. Liu, **J. Zhang**, X. Yu, S. Ding, Y. Luo, J. Gu, P. Shum, L. Liu. Dual spectrometer system with spectral compounding for 1- μ m optical coherence tomography in vivo. *Optics Letters*, 2014, 39(23): 6727-6730.
6. S. Ma, T. Ye, T. Zhang, Z. Wang, K. Li, M. Chen, **J. Zhang**, Z. Wang, S. Ramakrishna, and L. Wei, Highly oriented electrospun P(VDF-TrFE) fibers via mechanical stretching for wearable motion sensing, *Advanced Materials Technologies*, in the press, (2018).
7. K. Li, N. Zhang, T. Zhang, Z. Wang, M. Chen, T. Wu, S. Ma, M. Zhang, **J. Zhang**, Dinish U. S, P. Shum, M. Olivo, and L. Wei, Formation of ultra-flexible, conformal, and nano-patterned photonic surfaces via polymer cold-drawing, *Journal of Materials Chemistry C* 6, 4649-4657 (2018).
8. M. Zhang, K. Li, T. Zhang, P. Shum, Z. Wang, Z. Wang, N. Zhang, **J. Zhang**, T. Wu, and L. Wei, Electron-rich two-dimensional molybdenum trioxides for highly integrated plasmonic biosensing, *ACS Photonics* 5, 347-352 (2018).
9. M. Chen, J. Xia, J. Zhou, Q. Zeng, K. Li, K. Fujisawa, W. Fu, T. Zhang, **J. Zhang**, Z. Wang, Z. Wang, X. Jia, M. Terrones, Z. Shen, Z. Liu, and L. Wei, Ordered and

atomically perfect fragmentation of layered transition metal dichalcogenides via mechanical instabilities, *ACS Nano* 11, 9191-9199 (2017).

10. Y. He, Y. Sun, Z. Wang, S. Ma, N. Zhang, **J. Zhang**, S. Soh, and L. Wei, Pristine graphene oxide film-based contactless actuators driven by electrostatic force, *Journal of Materials Chemistry C* 5, 9534-9539 (2017).
11. K. Li, T. Zhang, N. Zhang, M. Zhang, **J. Zhang**, T. Wu, S. Ma, J. Wu, M. Chen, Y. He, and L. Wei, Integrated liquid crystal photonic bandgap fiber devices, *Frontiers of Optoelectronics* 9, 466-482 (2016). **Invited Review**.

Conference:

1. **J. Zhang**, K. Li, T. Zhang, and L. Wei, Laser Induced In-fiber Capillary Instabilities for Precise and Scalable Microsphere Fabrication, in *Conference on Lasers and Electro-Optics (CLEO)* pp. 1-2 (2016).
2. **J. Zhang**, K. Li, M. Zhang T. Zhang, and L. Wei, High-Q Silicon Microsphere Whispering Gallery Mode Resonator Fabricated by Laser Induced In-Fiber Capillary Instability, in *Lasers and Electro-Optics Pacific Rim (CLEO-PR)* pp. 1-3 (2017).
3. D. Cui, X. Liu, **J. Zhang**, X. Yu, D. Sun., Y. Luo, J. Gu, P. Shum, and L. Liu, One-Micron Resolution Optical Coherence Tomography (OCT) in Vivo for Cellular Level Imaging, In *Optical Coherence Tomography and Coherence Domain Optical Methods in Biomedicine XIX*, vol. 9312, p. 93123R, International Society for Optics and Photonics (2015).

Bibliography

1. A. C. Peacock, J. R. Sparks, and N. Healy, "Semiconductor optical fibres: progress and opportunities," *Laser & Photonics Reviews* **8**, 53-72 (2014).
2. L. Wei, C. Hou, E. Levy, G. Lestoquoy, A. Gumennik, A. F. Abouraddy, J. D. Joannopoulos, and Y. Fink, "Optoelectronic Fibers via Selective Amplification of In-Fiber Capillary Instabilities," *Advanced Materials* **29**(2017).
3. M. Kanik, M. Marcali, M. Yunusa, C. Elbuken, and M. Bayindir, "Continuous triboelectric power harvesting and biochemical sensing inside poly (vinylidene fluoride) hollow fibers using microfluidic droplet generation," *Advanced Materials Technologies* **1**, 1600190 (2016).
4. E. Ozgur, P. Toren, O. Aktas, E. Huseyinoglu, and M. Bayindir, "Label-Free Biosensing with High Selectivity in Complex Media using Microtoroidal Optical Resonators," *Scientific Reports* **5**, 13173 (2015).
5. A. Gumennik, E. C. Levy, B. Grena, C. Hou, M. Rein, A. F. Abouraddy, J. D. Joannopoulos, and Y. Fink, "Confined in-fiber solidification and structural control of silicon and silicon-germanium microparticles," *Proceedings of the National Academy of Sciences of the United States of America* **114**, 7240-7245 (2017).
6. C. Hou, X. Jia, L. Wei, S.-C. Tan, X. Zhao, J. D. Joannopoulos, and Y. Fink, "Crystalline silicon core fibres from aluminum core preforms," *Nature Communications* **6**, 6248 (2015).
7. S. Shabahang, G. Tao, J. J. Kaufman, Y. Qiao, L. Wei, T. Bouchenot, A. P. Gordon, Y. Fink, Y. Bai, R. S. Hoy, and A. F. Abouraddy, "Controlled fragmentation of multimaterial fibres and films via polymer cold-drawing," *Nature* **534**, 529-533 (2016).
8. A. Gumennik, L. Wei, G. Lestoquoy, A. M. Stolyarov, X. Jia, P. H. Rekemeyer, M. J. Smith, X. Liang, B. J.-B. Grena, and S. G. Johnson, "Silicon-in-silica spheres via axial thermal gradient in-fibre capillary instabilities," *Nature Communications* **4**, 2216 (2013).
9. O. Aktas, E. Ozgur, O. Tobail, M. Kanik, E. Huseyinoglu, and M. Bayindir, "A new route for fabricating on - chip chalcogenide microcavity resonator arrays," *Advanced Optical Materials* **2**, 618-625 (2014).
10. N. Healy, M. Fokine, Y. Franz, T. Hawkins, M. Jones, J. Ballato, A. C. Peacock, and U. J. Gibson, "CO₂Laser-Induced Directional Recrystallization to Produce Single Crystal Silicon-Core Optical Fibers with Low Loss," *Advanced Optical Materials* **4**, 1004-1008 (2016).
11. A. C. Peacock, N. Healy, F. Suhailin, S. Mailis, J. Ballato, and U. Gibson, "Crystalline core silicon fibers for optoelectronic applications," in *Integrated Photonics Research, Silicon and Nanophotonics*, (Optical Society of America, 2016), IM3A. 1.

12. J. C. Splitstoser, T. D. Dillehay, J. Wouters, and A. Claro, "Early pre-Hispanic use of indigo blue in Peru," *Science Advances* **2**(2016).
13. K. Kao and G. A. Hockham, "Dielectric-fibre surface waveguides for optical frequencies," in *Proceedings of the Institution of Electrical Engineers*, (IET, 1966), 1151-1158.
14. G. Tao, A. M. Stolyarov, and A. F. Abouraddy, "Multimaterial Fibers," *International Journal of Applied Glass Science* **3**, 349-368 (2012).
15. A. Gumennik, A. M. Stolyarov, B. R. Schell, C. Hou, G. Lestoquoy, F. Sorin, W. McDaniel, A. Rose, J. D. Joannopoulos, and Y. Fink, "All-in-fiber chemical sensing," *Advanced Materials* **24**, 6005-6009 (2012).
16. M. Bayindir, F. Sorin, A. F. Abouraddy, J. Viens, S. D. Hart, J. D. Joannopoulos, and Y. Fink, "Metal-insulator-semiconductor optoelectronic fibres," *Nature* **431**, 826 (2004).
17. M. Rein, E. Levy, A. Gumennik, A. F. Abouraddy, J. Joannopoulos, and Y. Fink, "Self-assembled fibre optoelectronics with discrete translational symmetry," *Nature Communications* **7**, 12807 (2016).
18. J. S. Sanghera, L. Brandon Shaw, and I. D. Aggarwal, "Chalcogenide Glass-Fiber-Based Mid-IR Sources and Applications," *IEEE Journal of Selected Topics in Quantum Electronics* **15**, 114-119 (2009).
19. S. Shabahang, G. Tao, J. J. Kaufman, and A. F. Abouraddy, "Dispersion characterization of chalcogenide bulk glass, composite fibers, and robust nanotapers," *Journal of the Optical Society of America B* **30**(2013).
20. A. Canales, X. Jia, U. P. Froriep, R. A. Koppes, C. M. Tringides, J. Selvidge, C. Lu, C. Hou, L. Wei, Y. Fink, and P. Anikeeva, "Multifunctional fibers for simultaneous optical, electrical and chemical interrogation of neural circuits in vivo," *Nature Biotechnology* **33**, 277-284 (2015).
21. Y. Guo, S. Jiang, B. J. B. Grena, I. F. Kimbrough, E. G. Thompson, Y. Fink, H. Sontheimer, T. Yoshinobu, and X. Jia, "Polymer Composite with Carbon Nanofibers Aligned during Thermal Drawing as a Microelectrode for Chronic Neural Interfaces," *ACS Nano* **11**, 6574-6585 (2017).
22. F. Yang, "Viscosity measurement of polycarbonate by using a penetration viscometer," *Polymer Engineering & Science* **37**, 101-104 (1997).
23. A. Tverjanovich, "Temperature dependence of the viscosity of chalcogenide glass-forming melts," *Glass Physics and Chemistry* **29**, 532-536 (2003).
24. A. Sipp, D. R. Neuville, and P. Richet, "Viscosity, configurational entropy and relaxation kinetics of borosilicate melts," *Journal of Non-Crystalline Solids* **211**, 281-293 (1997).
25. R. Setnescu, I. Bancuta, T. Setnescu, V. Cimpoca, S. Jipa, and I. V. Popescu, "Thermal characterization of semiconductor Bi₂Te₃ materials using DSC," *Journal of Science and Arts* **1**, 95-102 (2010).
26. R. H. Doremus, "Viscosity of silica," *Journal of Applied Physics* **92**, 7619-7629 (2002).

27. M. J. Assael, A. E. Kalyva, K. D. Antoniadis, R. Michael Banish, I. Egry, J. Wu, E. Kaschnitz, and W. A. Wakeham, "Reference data for the density and viscosity of liquid copper and liquid tin," *Journal of Physical and Chemical Reference Data* **39**, 033105 (2010).
28. D. Ofte, "The viscosities of liquid uranium, gold and lead," *Journal of nuclear materials* **22**, 28-32 (1967).
29. Y. Sato, Y. Kameda, T. Nagasawa, T. Sakamoto, S. Moriguchi, T. Yamamura, and Y. Waseda, "Viscosity of molten silicon and the factors affecting measurement," *Journal of Crystal Growth* **249**, 404-415 (2003).
30. Y. Sato, T. Nishizuka, T. Tachikawa, M. Hoshi, T. Yamamura, and Y. Waseda, "Viscosity and density of molten germanium," *High Temperatures High Pressures(UK)* **32**, 253-260 (2000).
31. B. Temelkuran, S. D. Hart, G. Benoit, J. D. Joannopoulos, and Y. Fink, "Wavelength-scalable hollow optical fibres with large photonic bandgaps for CO₂ laser transmission," *Nature* **420**, 650 (2002).
32. Z. Ruff, D. Shemuly, X. Peng, O. Shapira, Z. Wang, and Y. Fink, "Polymer-composite fibers for transmitting high peak power pulses at 1.55 microns," *Optics Express* **18**, 15697-15703 (2010).
33. A. Abouraddy, M. Bayindir, G. Benoit, S. Hart, K. Kuriki, N. Orf, O. Shapira, F. Sorin, B. Temelkuran, and Y. Fink, "Towards multimaterial multifunctional fibres that see, hear, sense and communicate," *Nature materials* **6**, 336 (2007).
34. O. Shapira, K. Kuriki, N. D. Orf, A. F. Abouraddy, G. Benoit, J. F. Viens, A. Rodriguez, M. Ibanescu, J. D. Joannopoulos, Y. Fink, and M. M. Brewster, "Surface-emitting fiber lasers," *Optics Express* **14**, 3929-3935 (2006).
35. A. M. Stolyarov, L. Wei, F. Sorin, G. Lestoquoy, J. D. Joannopoulos, and Y. Fink, "Fabrication and characterization of fibers with built-in liquid crystal channels and electrodes for transverse incident-light modulation," *Applied Physics Letters* **101** (2012).
36. A. M. Stolyarov, L. Wei, O. Shapira, F. Sorin, S. L. Chua, J. D. Joannopoulos, and Y. Fink, "Microfluidic directional emission control of an azimuthally polarized radial fibre laser," *Nature Photonics* **6**, 229-233 (2012).
37. N. Zhang, H. Liu, A. M. Stolyarov, T. Zhang, K. Li, P. P. Shum, Y. Fink, X. W. Sun, and L. Wei, "Azimuthally Polarized Radial Emission from a Quantum Dot Fiber Laser," *ACS Photonics* **3**, 2275-2279 (2016).
38. A. M. Stolyarov, A. Gumennik, W. McDaniel, O. Shapira, B. Schell, F. Sorin, K. Kuriki, G. Benoit, A. Rose, J. D. Joannopoulos, and Y. Fink, "Enhanced chemiluminescent detection scheme for trace vapor sensing in pneumatically-tuned hollow core photonic bandgap fibers," *Optics Express* **20**, 12407-12415 (2012).
39. A. F. Abouraddy, M. Bayindir, G. Benoit, S. D. Hart, K. Kuriki, N. Orf, O. Shapira, F. Sorin, B. Temelkuran, and Y. Fink, "Towards multimaterial multifunctional fibres that see, hear, sense and communicate," *Nature Materials* **6**, 336 (2007).

40. M. Bayindir, O. Shapira, D. Saygin-Hinczewski, J. Viens, A. F. Abouraddy, J. D. Joannopoulos, and Y. Fink, "Integrated fibres for self-monitored optical transport," *Nature Materials* **4**, 820 (2005).
41. F. Sorin, O. Shapira, A. F. Abouraddy, M. Spencer, N. D. Orf, J. D. Joannopoulos, and Y. Fink, "Exploiting collective effects of multiple optoelectronic devices integrated in a single fiber," *Nano letters* **9**, 2630-2635 (2009).
42. F. Sorin, A. F. Abouraddy, N. Orf, O. Shapira, J. Viens, J. Arnold, J. D. Joannopoulos, and Y. Fink, "Multimaterial photodetecting fibers: a geometric and structural study," *Advanced Materials* **19**, 3872-3877 (2007).
43. F. Sorin, G. Lestoquoy, S. Danto, J. D. Joannopoulos, and Y. Fink, "Resolving optical illumination distributions along an axially symmetric photodetecting fiber," *Optics Express* **18**, 24264-24275 (2010).
44. A. F. Abouraddy, O. Shapira, M. Bayindir, J. Arnold, F. Sorin, D. S. Hinczewski, J. D. Joannopoulos, and Y. Fink, "Large-scale optical-field measurements with geometric fibre constructs," *Nat Mater* **5**, 532-536 (2006).
45. M. Lee, C. Y. Chen, S. Wang, S. N. Cha, Y. J. Park, J. M. Kim, L. J. Chou, and Z. L. Wang, "A hybrid piezoelectric structure for wearable nanogenerators," *Advanced Materials* **24**, 1759-1764 (2012).
46. S. J. Kim, J. H. We, and B. J. Cho, "A wearable thermoelectric generator fabricated on a glass fabric," *Energy & Environmental Science* **7**, 1959-1965 (2014).
47. K. N. Kim, J. Chun, J. W. Kim, K. Y. Lee, J.-U. Park, S.-W. Kim, Z. L. Wang, and J. M. Baik, "Highly stretchable 2D fabrics for wearable triboelectric nanogenerator under harsh environments," *ACS nano* **9**, 6394-6400 (2015).
48. D. A. Skoog, F. J. Holler, and S. R. Crouch, *Instrumental Analysis* (Brooks/Cole, Cengage Learning Belmont, 2007).
49. P. Skládal, "Piezoelectric biosensors," *TrAC Trends in Analytical Chemistry* **79**, 127-133 (2016).
50. Z. Liu, X. Zhang, Y. Mao, Y. Zhu, Z. Yang, C. T. Chan, and P. Sheng, "Locally resonant sonic materials," *Science* **289**, 1734-1736 (2000).
51. C. Lang, J. Fang, H. Shao, X. Ding, and T. Lin, "High-sensitivity acoustic sensors from nanofibre webs," *Nature Communications* **7**, 11108 (2016).
52. G. Ma, M. Yang, S. Xiao, Z. Yang, and P. Sheng, "Acoustic metasurface with hybrid resonances," *Nature Materials* **13**, 873 (2014).
53. S. Wang, T. Zhang, K. Li, S. Ma, M. Chen, P. Lu, and L. Wei, "Flexible piezoelectric fibers for acoustic sensing and positioning," *Advanced Electronic Materials* **3**, 1600449 (2017).
54. S. Egusa, Z. Wang, N. Chocat, Z. M. Ruff, A. M. Stolyarov, D. Shemuly, F. Sorin, P. T. Rakich, J. D. Joannopoulos, and Y. Fink, "Multimaterial piezoelectric fibres," *Nature Materials* **9**, 643 (2010).

55. N. Chocat, G. Lestoquoy, Z. Wang, D. M. Rodgers, J. D. Joannopoulos, and Y. Fink, "Piezoelectric fibers for conformal acoustics," *Advanced Materials* **24**, 5327-5332 (2012).
56. A. Shakouri, "Recent developments in semiconductor thermoelectric physics and materials," *Annual review of materials research* **41**, 399-431 (2011).
57. L. E. Bell, "Cooling, heating, generating power, and recovering waste heat with thermoelectric systems," *Science* **321**, 1457-1461 (2008).
58. G. J. Snyder and E. S. Toberer, "Complex thermoelectric materials," in *Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group* (World Scientific, 2011), pp. 101-110.
59. G. H. Kim, L. Shao, K. Zhang, and K. P. Pipe, "Engineered doping of organic semiconductors for enhanced thermoelectric efficiency," *Nature Materials* **12**, 719 (2013).
60. O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, and X. Crispin, "Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylene dioxythiophene)," *Nature Materials* **10**, 429 (2011).
61. T. Zhang, K. Li, C. Li, S. Ma, H. H. Hng, and L. Wei, "Mechanically Durable and Flexible Thermoelectric Films from PEDOT: PSS/PVA/Bi_{0.5}Sb_{1.5}Te₃ Nanocomposites," *Advanced Electronic Materials* **3**, 1600554 (2017).
62. S. H. Park, S. Jo, B. Kwon, F. Kim, H. W. Ban, J. E. Lee, D. H. Gu, S. H. Lee, Y. Hwang, J.-S. Kim, D.-B. Hyun, S. Lee, K. J. Choi, W. Jo, and J. S. Son, "High-performance shape-engineerable thermoelectric painting," *Nature Communications* **7**, 13403 (2016).
63. J. P. Rojas, D. Conchouso, A. Arevalo, D. Singh, I. G. Foulds, and M. M. Hussain, "based origami flexible and foldable thermoelectric nanogenerator," *Nano Energy* **31**, 296-301 (2017).
64. T. Zhang, K. Li, J. Zhang, M. Chen, Z. Wang, S. Ma, N. Zhang, and L. Wei, "High-performance, flexible, and ultralong crystalline thermoelectric fibers," *Nano Energy* **41**, 35-42 (2017).
65. B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, and D. Vashaee, "High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys," *Science* **320**, 634-638 (2008).
66. W. R. Harper, *Contact and frictional electrification* (Clarendon Press, 1967).
67. X. Shen, A. E. Wang, R. M. Sankaran, and D. J. Lacks, "First-principles calculation of contact electrification and validation by experiment," *Journal of Electrostatics* **82**, 11-16 (2016).
68. Z. L. Wang, "Triboelectric nanogenerators as new energy technology for self-powered systems and as active mechanical and chemical sensors," *ACS Nano* **7**, 9533-9557 (2013).

69. G. Zhu, J. Chen, T. Zhang, Q. Jing, and Z. L. Wang, "Radial-arrayed rotary electrification for high performance triboelectric generator," *Nature Communications* **5**, 3426 (2014).
70. C. Xu and Z. L. Wang, "Compact hybrid cell based on a convoluted nanowire structure for harvesting solar and mechanical energy," *Advanced Materials* **23**, 873-877 (2011).
71. M. Kanik, M. G. Say, B. Daglar, A. F. Yavuz, M. H. Dolas, M. M. El - Ashry, and M. Bayindir, "A motion - and sound - activated, 3d - printed, chalcogenide - based triboelectric nanogenerator," *Advanced Materials* **27**, 2367-2376 (2015).
72. N. D. Orf, O. Shapira, F. Sorin, S. Danto, M. A. Baldo, J. D. Joannopoulos, and Y. Fink, "Fiber draw synthesis," *Proceedings of the National Academy of Sciences* **108**, 4743-4747 (2011).
73. E. Gavrushchuk, "Polycrystalline zinc selenide for IR optical applications," *Inorganic Materials* **39**, 883-899 (2003).
74. I. Sou, Z. Ma, and G. Wong, "Photoresponse studies of ZnSSe visible-blind ultraviolet detectors: A comparison to ZnSTe detectors," *Applied Physics Letters* **75**, 3707-3709 (1999).
75. C. Hou, X. Jia, L. Wei, A. M. Stolyarov, O. Shapira, J. D. Joannopoulos, and Y. Fink, "Direct Atomic-Level Observation and Chemical Analysis of ZnSe Synthesized by in Situ High-Throughput Reactive Fiber Drawing," *Nano Letters* **13**, 975-979 (2013).
76. A. Ricciardi, M. Consales, G. Quero, A. Crescitelli, E. Esposito, and A. Cusano, "Lab-on-fiber devices as an all around platform for sensing," *Optical Fiber Technology* **19**, 772-784 (2013).
77. D. L. Chandler, "Introducing the latest in textiles: Soft hardware" (2018), retrieved <http://news.mit.edu/2018/optoelectronic-diodes-fibers-fabrics-soft-hardware-0808>.
78. M. Rein, V. D. Favrod, C. Hou, T. Khudiyev, A. Stolyarov, J. Cox, C.-C. Chung, C. Chhav, M. Ellis, and J. Joannopoulos, "Diode fibres for fabric-based optical communications," *Nature* **560**, 214 (2018).
79. A. Holtmaat and K. Svoboda, "Experience-dependent structural synaptic plasticity in the mammalian brain," *Nature Reviews Neuroscience* **10**, 647 (2009).
80. F. Zhang, A. M. Aravanis, A. Adamantidis, L. de Lecea, and K. Deisseroth, "Circuit-breakers: optical technologies for probing neural signals and systems," *Nature Reviews Neuroscience* **8**, 577 (2007).
81. S. Ramirez, X. Liu, P.-A. Lin, J. Suh, M. Pignatelli, R. L. Redondo, T. J. Ryan, and S. Tonegawa, "Creating a false memory in the hippocampus," *Science* **341**, 387-391 (2013).
82. P. Znamenskiy and A. M. Zador, "Corticostriatal neurons in auditory cortex drive decisions during auditory discrimination," *Nature* **497**, 482 (2013).

83. N. Zhang, G. Humbert, T. Gong, P. P. Shum, K. Li, J.-L. Auguste, Z. Wu, D. J. J. Hu, F. Luan, and Q. X. Dinh, "Side-channel photonic crystal fiber for surface enhanced Raman scattering sensing," *Sensors and Actuators B: Chemical* **223**, 195-201 (2016).
84. T. Gong, N. Zhang, K. V. Kong, D. Goh, C. Ying, J. L. Auguste, P. P. Shum, L. Wei, G. Humbert, and K. T. Yong, "Rapid SERS monitoring of lipid - peroxidation - derived protein modifications in cells using photonic crystal fiber sensor," *Journal of Biophotonics* **9**, 32-37 (2016).
85. N. M. Y. Zhang, K. Li, N. Zhang, Y. Zheng, T. Zhang, M. Qi, P. Shum, and L. Wei, "Highly sensitive gas refractometers based on optical microfiber modal interferometers operating at dispersion turning point," *Optics Express* **26**, 29148-29158 (2018).
86. N. Zhang, K. Li, Y. Cui, Z. Wu, P. P. Shum, J.-L. Auguste, X. Q. Dinh, G. Humbert, and L. Wei, "Ultra-sensitive chemical and biological analysis via specialty fibers with built-in microstructured optofluidic channels," *Lab on a Chip* **18**, 655-661 (2018).
87. N. M. Y. Zhang, K. Li, T. Zhang, P. Shum, Z. Wang, Z. Wang, N. Zhang, J. Zhang, T. Wu, and L. Wei, "Electron-Rich Two-Dimensional Molybdenum Trioxides for Highly Integrated Plasmonic Biosensing," *ACS Photonics* **5**, 347-352 (2017).
88. A. Yildirim, M. Vural, M. Yaman, and M. Bayindir, "Bioinspired Optoelectronic Nose with Nanostructured Wavelength - Scalable Hollow - Core Infrared Fibers," *Advanced Materials* **23**, 1263-1267 (2011).
89. T. A. Dickinson, J. White, J. S. Kauer, and D. R. Walt, "A chemical-detecting system based on a cross-reactive optical sensor array," *Nature* **382**, 697 (1996).
90. M. S. Meaney and V. L. McGuffin, "Luminescence-based methods for sensing and detection of explosives," *Analytical and Bioanalytical Chemistry* **391**, 2557 (2008).
91. R. Schulte-Ladbeck, M. Vogel, and U. Karst, "Recent methods for the determination of peroxide-based explosives," *Analytical and Bioanalytical Chemistry* **386**, 559-565 (2006).
92. A. Kitai, *Principles of Solar Cells, LEDs and Diodes: The role of the PN junction* (John Wiley & Sons, 2011).
93. G. Cao, *Nanostructures & nanomaterials: synthesis, properties & applications* (Imperial college press, 2004).
94. W. Lu and C. M. Lieber, "Nanoelectronics from the bottom up," in *Nanoscience And Technology: A Collection of Reviews from Nature Journals* (World Scientific, 2010), pp. 137-146.
95. Z. L. Wang, "Functional oxide nanobelts: materials, properties and potential applications in nanosystems and biotechnology," *Annual Review of Physical Chemistry* **55**, 159-196 (2004).

96. W.-Y. Li, L.-N. Xu, and J. Chen, "Co₃O₄ nanomaterials in lithium - ion batteries and gas sensors," *Advanced Functional Materials* **15**, 851-857 (2005).
97. D. Deng, J.-C. Nave, X. Liang, S. Johnson, and Y. Fink, "Exploration of in-fiber nanostructures from capillary instability," *Optics Express* **19**, 16273-16290 (2011).
98. T. Khudiyev, O. Tobail, and M. Bayindir, "Tailoring self-organized nanostructured morphologies in kilometer-long polymer fiber," *Scientific Reports* **4**, 4864 (2014).
99. D. Deng, N. Orf, S. Danto, A. Abouraddy, J. Joannopoulos, and Y. Fink, "Processing and properties of centimeter-long, in-fiber, crystalline-selenium filaments," *Applied Physics Letters* **96**, 023102 (2010).
100. S. Haefner, M. Benzaquen, O. Bäümchen, T. Salez, R. Peters, J. D. McGraw, K. Jacobs, E. Raphaël, and K. Dalnoki-Veress, "Influence of slip on the Plateau-Rayleigh instability on a fibre," *Nature Communications* **6**, 7409 (2015).
101. S. Shabahang, J. Kaufman, D. Deng, and A. Abouraddy, "Observation of the Plateau-Rayleigh capillary instability in multi-material optical fibers," *Applied Physics Letters* **99**, 161909 (2011).
102. J. J. Kaufman, G. Tao, S. Shabahang, E. H. Banaei, D. S. Deng, X. Liang, S. G. Johnson, Y. Fink, and A. F. Abouraddy, "Structured spheres generated by an in-fibre fluid instability," *Nature* **487**, 463-467 (2012).
103. J. Kaufman, "Multifunctional, Multimaterial Particle Fabrication Via an In-Fiber Fluid Instability," (2014).
104. F. H. Suhailin, N. Healy, M. Sumetsky, J. Ballato, A. Dibbs, U. Gibson, and A. C. Peacock, "Kerr nonlinear switching in a core-shell microspherical resonator fabricated from the silicon fiber platform," in *CLEO: Science and Innovations*, (Optical Society of America, 2015), STh1O. 2.
105. N. Vukovic, N. Healy, F. Suhailin, P. Mehta, T. Day, J. Badding, and A. Peacock, "Ultrafast optical control using the Kerr nonlinearity in hydrogenated amorphous silicon microcylindrical resonators," *Scientific Reports* **3**, 2885 (2013).
106. D. S. Deng, N. D. Orf, S. Danto, A. F. Abouraddy, J. D. Joannopoulos, and Y. Fink, "Processing and properties of centimeter-long, in-fiber, crystalline-selenium filaments," *Applied Physics Letters* **96**(2010).
107. F. A. Martinsen, B. K. Smeltzer, M. Nord, T. Hawkins, J. Ballato, and U. J. Gibson, "Silicon-core glass fibres as microwire radial-junction solar cells," *Scientific Reports* **4**, 6283 (2014).
108. L. D. Zhao, S. H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, "Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals," *Nature* **508**, 373-377 (2014).
109. D. A. Coucheron, M. Fokine, N. Patil, D. W. Breiby, O. T. Buset, N. Healy, A. C. Peacock, T. Hawkins, M. Jones, J. Ballato, and U. J. Gibson, "Laser

- recrystallization and inscription of compositional microstructures in crystalline SiGe-core fibres," *Nature Communications* **7**, 13265 (2016).
110. X. Ji, S. Lei, S.-Y. Yu, H. Y. Cheng, W. Liu, N. Poilvert, Y. Xiong, I. Dabo, S. E. Mohny, and J. V. Badding, "Single-crystal silicon optical fiber by direct laser crystallization," *ACS Photonics* **4**, 85-92 (2016).
 111. N. F. Baril, R. He, T. D. Day, J. R. Sparks, B. Keshavarzi, M. Krishnamurthi, A. Borhan, V. Gopalan, A. C. Peacock, and N. Healy, "Confined high-pressure chemical deposition of hydrogenated amorphous silicon," *Journal of the American Chemical Society* **134**, 19-22 (2011).
 112. N. Granzow, M. Schmidt, W. Chang, L. Wang, Q. Coulombier, J. Troles, P. Toupin, I. Hartl, K. Lee, and M. Fermann, "Mid-infrared supercontinuum generation in As₂S₃-silica "nano-spike" step-index waveguide," *Optics Express* **21**, 10969-10977 (2013).
 113. A. C. Peacock and N. Healy, "Semiconductor optical fibres for infrared applications: A review," *Semiconductor Science and Technology* **31**, 103004 (2016).
 114. J. Ballato, T. Hawkins, P. Foy, B. Yazgan-Kokuoz, C. McMillen, L. Burka, S. Morris, R. Stolen, and R. Rice, "Advancements in semiconductor core optical fiber," *Optical Fiber Technology* **16**, 399-408 (2010).
 115. J. Ballato, T. Hawkins, P. Foy, C. McMillen, L. Burka, J. Reppert, R. Podila, A. Rao, and R. R. Rice, "Binary III-V semiconductor core optical fiber," *Optics Express* **18**, 4972-4979 (2010).
 116. W. Pfann, "Techniques of zone melting and crystal growing," in *Solid State Physics* (Elsevier, 1957), pp. 423-521.
 117. X. Ji, R. L. Page, S. Chaudhuri, W. Liu, S.-Y. Yu, S. E. Mohny, J. V. Badding, and V. Gopalan, "Single-Crystal Germanium Core Optoelectronic Fibers," *Advanced Optical Materials* **5**(2017).
 118. N. Healy, S. Mailis, N. M. Bulgakova, P. J. Sazio, T. D. Day, J. R. Sparks, H. Y. Cheng, J. V. Badding, and A. C. Peacock, "Extreme electronic bandgap modification in laser-crystallized silicon optical fibres," *Nature Materials* **13**, 1122-1127 (2014).
 119. R. J. Knrpnrncr, "Crystal growth from the melt: a review," *American Mineralogist* **60**, 798-814 (1975).
 120. A. Sebastian, M. Le Gallo, and D. Krebs, "Crystal growth within a phase change memory cell," *Nature Communications* **5**, 4314 (2014).
 121. T. Van Buuren, L. Dinh, L. Chase, W. Siekhaus, and L. J. Terminello, "Changes in the electronic properties of Si nanocrystals as a function of particle size," *Physical Review Letters* **80**, 3803 (1998).
 122. P. Wang, T. Lee, M. Ding, A. Dhar, T. Hawkins, P. Foy, Y. Semenova, Q. Wu, J. Sahu, and G. Farrell, "Germanium microsphere high-Q resonator," *Optics Letters* **37**, 728-730 (2012).

123. J.-H. Park, L. Gu, G. Von Maltzahn, E. Ruoslahti, S. N. Bhatia, and M. J. Sailor, "Biodegradable luminescent porous silicon nanoparticles for in vivo applications," *Nature Materials* **8**, 331 (2009).
124. A. L. Watts, N. Singh, C. G. Poulton, E. C. Magi, I. V. Kabakova, D. D. Hudson, and B. J. Eggleton, "Photoinduced axial quantization in chalcogenide microfiber resonators," *JOSA B* **30**, 3249-3253 (2013).
125. J. Ward and O. Benson, "WGM microresonators: sensing, lasing and fundamental optics with microspheres," *Laser & Photonics Reviews* **5**, 553-570 (2011).
126. K. Taira and J. Nakata, "Silicon cells: catching rays," *Nature Photonics* **4**, 602-603 (2010).
127. H. Kohno and S. Takeda, "Self-organized chain of crystalline-silicon nanospheres," *Applied Physics Letters* **73**, 3144-3146 (1998).
128. N. Rao, N. Tymiak, J. Blum, A. Neuman, H. Lee, S. Girshick, P. McMurry, and J. Heberlein, "Hypersonic plasma particle deposition of nanostructured silicon and silicon carbide," *Journal of Aerosol Science* **29**, 707-720 (1998).
129. R. G. Hobbs, N. Petkov, and J. D. Holmes, "Semiconductor nanowire fabrication by bottom-up and top-down paradigms," *Chemistry of Materials* **24**, 1975-1991 (2012).
130. A. Wolfsteller, N. Geyer, T.-K. Nguyen-Duc, P. D. Kanungo, N. Zakharov, M. Reiche, W. Erfurth, H. Blumtritt, S. Kalem, and P. Werner, "Comparison of the top-down and bottom-up approach to fabricate nanowire-based silicon/germanium heterostructures," *Thin Solid Films* **518**, 2555-2561 (2010).
131. Y. Wang and Y. Xia, "Bottom-up and top-down approaches to the synthesis of monodispersed spherical colloids of low melting-point metals," *Nano letters* **4**, 2047-2050 (2004).
132. R. d. Gennes, F. Brochard-Wyart, D. Quere, and B. Widom, "Books-Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves," *Physics Today* **57**, 63 (2004).
133. L. Rayleigh, "On the instability of jets," *Proceedings of the London mathematical society* **1**, 4-13 (1878).
134. L. Rayleigh, "On the capillary phenomena of jets," *Proceedings of the Royal Society of London* **29**, 71-97 (1879).
135. L. Rayleigh, "XX. On the equilibrium of liquid conducting masses charged with electricity," *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **14**, 184-186 (1882).
136. S. Tomotika, "On the instability of a cylindrical thread of a viscous liquid surrounded by another viscous fluid," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **150**, 322-337 (1935).
137. X. Liang, D. Deng, J.-C. Nave, and S. G. Johnson, "Linear stability analysis of capillary instabilities for concentric cylindrical shells," *Journal of Fluid Mechanics* **683**, 235-262 (2011).

138. T. Frolov, W. C. Carter, and M. Asta, "Capillary instability in nanowire geometries," *Nano letters* **14**, 3577-3581 (2014).
139. S. Chandrasekhar, "Hydrodynamics and Hydrodynamic stability," Clarendon, Oxford (1961).
140. J. Zhang, K. Li, T. Zhang, and L. Wei, "Laser Induced In-fiber Capillary Instabilities for Precise and Scalable Microsphere Fabrication," in *Conference on Lasers and Electro-Optics*, OSA Technical Digest (online) (Optical Society of America, 2016), JTh2A.69.
141. T. Khudiyev, T. Dogan, and M. Bayindir, "Biomimicry of multifunctional nanostructures in the neck feathers of mallard (*Anas platyrhynchos* L.) drakes," *Scientific Reports* **4**(2014).
142. L. Xiao, N. Healy, Z. Webber, T. Hawkins, M. Jones, J. Ballato, U. Gibson, and A. Peacock, "In-fiber Silicon Microspheres," in *Asia Communications and Photonics Conference*, (Optical Society of America, 2015), ASu5C. 1.
143. X. Dai, G. G. Wildgoose, C. Salter, A. Crossley, and R. G. Compton, "Electroanalysis using macro-, micro-, and nanochemical architectures on electrode surfaces. Bulk surface modification of glassy carbon microspheres with gold nanoparticles and their electrical wiring using carbon nanotubes," *Analytical Chemistry* **78**, 6102-6108 (2006).
144. W. Yan, Y. Qu, T. D. Gupta, A. Darga, D. T. Nguyen, A. G. Page, M. Rossi, M. Ceriotti, and F. Sorin, "Semiconducting Nanowire - Based Optoelectronic Fibers," *Advanced Materials* (2017).
145. P. Dharmaiah, H.-S. Kim, C.-H. Lee, and S.-J. Hong, "Influence of powder size on thermoelectric properties of p-type 25% Bi₂Te₃ 75% Sb₂Te₃ alloys fabricated using gas-atomization and spark-plasma sintering," *Journal of Alloys and Compounds* **686**, 1-8 (2016).
146. A. Yadav, K. Pipe, and M. Shtein, "Fiber-based flexible thermoelectric power generator," *Journal of Power Sources* **175**, 909-913 (2008).
147. C. Kinoshita, H. Teng, and S. Masutani, "A study of the instability of liquid jets and comparison with Tomotika's analysis," *International Journal of Multiphase Flow* **20**, 523-533 (1994).
148. L. W. da Silva and M. Kaviani, "Micro-thermoelectric cooler: interfacial effects on thermal and electrical transport," *International Journal of Heat and Mass Transfer* **47**, 2417-2435 (2004).
149. J. H. Hilbing and S. D. Heister, "Droplet size control in liquid jet breakup," *Physics of Fluids* **8**, 1574-1581 (1996).
150. N. N. Mansour and T. S. Lundgren, "Satellite formation in capillary jet breakup," *Physics of Fluids A: Fluid Dynamics* **2**, 1141-1144 (1990).
151. K. Li, G. Liu, Y. Wu, P. Hao, W. Zhou, and Z. Zhang, "Gold nanoparticle amplified optical microfiber evanescent wave absorption biosensor for cancer biomarker detection in serum," *Talanta* **120**, 419-424 (2014).

152. M. Kishi, H. Nemoto, T. Hamao, M. Yamamoto, S. Sudou, M. Mandai, and S. Yamamoto, "Micro thermoelectric modules and their application to wristwatches as an energy source," in *Thermoelectrics, 1999. Eighteenth International Conference on*, (IEEE, 1999), 301-307.
153. N. Vukovic, N. Healy, P. Horak, J. R. Sparks, P. J. A. Sazio, J. V. Badding, and A. C. Peacock, "Ultra-smooth microcylindrical resonators fabricated from the silicon optical fiber platform," *Applied Physics Letters* **99**, 031117 (2011).
154. C. A. Lin, J. H. Chen, and L. A. Wang, "High Q Si Microsphere Resonators Fabricated From Si-Cored Fibers for WGMs Excitation," *IEEE Photonics Technology Letters* **27**, 1355-1358 (2015).
155. Z.-G. Chen, X. Shi, L.-D. Zhao, and J. Zou, "High-performance SnSe thermoelectric materials: Progress and future challenge," *Progress in Materials Science* **97**, 283-346 (2018).
156. L. D. Zhao, G. Tan, S. Hao, J. He, Y. Pei, H. Chi, H. Wang, S. Gong, H. Xu, V. P. Dravid, C. Uher, G. J. Snyder, C. Wolverton, and M. G. Kanatzidis, "Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe," *Science* **351**, 141-144 (2016).
157. J. Zhang, K. Li, T. Zhang, P. J. S. Buenconsejo, M. Chen, Z. Wang, M. Zhang, Z. Wang, and L. Wei, "Laser - Induced In - Fiber Fluid Dynamical Instabilities for Precise and Scalable Fabrication of Spherical Particles," *Advanced Functional Materials* **27**(2017).
158. V. M. G. a. O. V. Situlina, "SnSe Viscosity Temperature Variation in Short rang Structure of Molten Germanium and Tin Selenide and Sulphide," *Russian Journal of Physical Chemistry* **44**, 1406-1409 (1970).
159. T. N. A. A.A. Aleksandrov, V.S. Okhotin, L. A. Razumelchenko, and Z. I. Panina, "SnSe viscosity investigation of the density and viscosity of melts fo the Tin selenide system," *High Temperature* **15**, 47-52 (1977).
160. L. D. Zhao, C. Chang, G. J. Tan, and M. G. Kanatzidis, "SnSe: a remarkable new thermoelectric material," *Energy & Environmental Science* **9**, 3044-3060 (2016).
161. M. Zanolto, C. Rios, R. Jacon, and R. Caram, "Evaluation of the solid/liquid interface undercooling during Sn-Se eutectic growth," *Materials Research* **1**, 05-10 (1998).
162. M. Straumanis, "The precision determination of lattice constants by the powder and rotating crystal methods and applications," *Journal of Applied Physics* **20**, 726-734 (1949).
163. A. Mariano and K. Chopra, "Polymorphism in some IV - VI compounds induced by high pressure and thin - film epitaxial growth," *Applied Physics Letters* **10**, 282-284 (1967).
164. M. Palatnik and V. Levitin, "X-Ray Diffraction Studies of Tin-Selenium, Zinc-Selenium, Cadmium-Selenium and Silver-Selenium Alloys," in *Dokl. Akad. Nauk SSSR* **96**, 975-978 (1954).

165. H. Chandrasekhar, R. Humphreys, U. Zwick, and M. Cardona, "Infrared and Raman spectra of the IV-VI compounds SnS and SnSe," *Physical Review B* **15**, 2177 (1977).
166. J. Zhang, H. Zhu, X. Wu, H. Cui, D. Li, J. Jiang, C. Gao, Q. Wang, and Q. Cui, "Plasma-assisted synthesis and pressure-induced structural transition of single-crystalline SnSe nanosheets," *Nanoscale* **7**, 10807-10816 (2015).
167. D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin, and S. R. Phillpot, "Nanoscale thermal transport," *Journal of Applied Physics* **93**, 793-818 (2003).
168. H. Zhang, X. Chen, Y.-D. Jho, and A. J. Minnich, "Temperature-dependent mean free path spectra of thermal phonons along the c-axis of graphite," *Nano Letters* **16**, 1643-1649 (2016).
169. F. Sun, X. Wang, M. Yang, Z. Chen, H. Zhang, and D. Tang, "Simultaneous measurement of thermal conductivity and specific heat in a single TDTR experiment," *International Journal of Thermophysics* **39**, 5 (2018).
170. D. Wang, W. He, C. Chang, G. Wang, J. Wang, and L.-D. Zhao, "Thermoelectric transport properties of rock-salt SnSe: first-principles investigation," *Journal of Materials Chemistry C* (2018).
171. G. D. Tang, Q. Wen, T. Yang, Y. Cao, W. Wei, Z. H. Wang, Z. D. Zhang, and Y. S. Li, "Rock-salt-type nanoprecipitates lead to high thermoelectric performance in undoped polycrystalline SnSe," *RSC Advances* **7**, 8258-8263 (2017).
172. Y. S. Zhang, S. Q. Hao, L. D. Zhao, C. Wolverton, and Z. Zeng, "Pressure induced thermoelectric enhancement in SnSe crystals," *Journal of Materials Chemistry A* **4**, 12073-12079 (2016).
173. D. D. Cuong, S. H. Rhim, J. H. Lee, and S. C. Hong, "Strain effect on electronic structure and thermoelectric properties of orthorhombic SnSe: A first principles study," *AIP Advances* **5**(2015).
174. C. L. Chen, H. Wang, Y. Y. Chen, T. Day, and G. J. Snyder, "Thermoelectric properties of p-type polycrystalline SnSe doped with Ag," *Journal of Materials Chemistry A* **2**, 11171-11176 (2014).
175. R. S. Jacobsen, K. N. Andersen, P. I. Borel, J. Fage-Pedersen, L. H. Frandsen, O. Hansen, M. Kristensen, A. V. Lavrinenko, G. Moulin, and H. Ou, "Strained silicon as a new electro-optic material," *Nature* **441**, 199 (2006).
176. Y. Sun, S. Thompson, and T. Nishida, "Physics of strain effects in semiconductors and metal-oxide-semiconductor-field-effect transistors," *Journal of Applied Physics* **101**, 104503 (2007).
177. B. Welber, C. Kim, M. Cardona, and S. Rodriguez, "Dependence of the indirect energy gap of silicon on hydrostatic pressure," *Solid State Communications* **17**, 1021-1024 (1975).
178. P. Michael, M. Raith, *Guide to thin section microscopy*, Second Edition ed. (2012).

179. Z. Sui, H. H. Burke, and I. P. Herman, "Raman scattering in germanium-silicon alloys under hydrostatic pressure," *Physical Review B* **48**, 2162 (1993).
180. M. Darif, N. Semmar, and F. Orléans Cedex, "Numerical Simulation of Si Nanosecond Laser Annealing by COMSOL Multiphysics," in *Proceedings of the COMSOL Conference 2008 Hannover*, 2008),
181. S. Chaudhuri, J. R. Sparks, X. Ji, M. Krishnamurthi, L. Shen, N. Healy, A. C. Peacock, V. Gopalan, and J. V. Badding, "Crystalline Silicon Optical Fibers with Low Optical Loss," *ACS Photonics* **3**, 378-384 (2016).
182. M. Borselli, K. Srinivasan, P. E. Barclay, and O. Painter, "Rayleigh scattering, mode coupling, and optical loss in silicon microdisks," *Applied Physics Letters* **85**, 3693-3695 (2004).
183. T. J. Johnson, M. Borselli, and O. Painter, "Self-induced optical modulation of the transmission through a high-Q silicon microdisk resonator," *Optics Express* **14**, 817-831 (2006).
184. N. Vukovic, N. Healy, P. Horak, J. R. Sparks, P. J. Sazio, J. V. Badding, and A. C. Peacock, "Ultra-smooth microcylindrical resonators fabricated from the silicon optical fiber platform," *Applied Physics Letters* **99**, 031117 (2011).
185. A. Taeb, M. A. Basha, S. Gigoyan, M. Marsden, and S. Safavi-Naeini, "Label-free DNA sensing using millimeter-wave silicon WGM resonator," *Optics Express* **21**, 19467-19472 (2013).
186. Y. O. Yilmaz, A. Demir, A. Kurt, and A. Serpenguzel, "Optical channel dropping with a silicon microsphere," *IEEE Photonics Technology Letters* **17**, 1662-1664 (2005).
187. U. Gökay, M. Zakwan, and A. Serpengüzel, "Spherical silicon optical resonators: Possible applications to biosensing," *The European Physical Journal Special Topics* **223**, 2003-2008 (2014).
188. E. Xifré-Pérez, J. Domenech, R. Fenollosa, P. Muñoz, J. Capmany, and F. Meseguer, "All silicon waveguide spherical microcavity coupler device," *Optics Express* **19**, 3185-3192 (2011).