Nanostructured Materials for Energy Generation and Storage

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Development of new energy generation and storage technologies is important for increasing the share of renewable energy sources and wider use of the plug-in electric vehicles. Thermo-electric energy conversion is suitable for the waste-heat recovery allowing for energy reuse. The limited use of thermoelectric generators is explained by the low efficiency energy conversion defined by the thermoelectric figure of merit ZT. The factor that limits the scalability of energy storage in reversible electrochemical cells is high Ohmic losses, which degrade the battery performance. In this dissertation, I investigate innovative approaches for increasing the efficiency of the thermoelectric energy generation and battery storage via the use of nanostructured materials. It was theoretically predicted that strong quantum confinement of charge carriers and acoustic phonons can lead to drastic enhancement of ZT. I have used graphene-like mechanical exfoliation of Bi$_2$Te$_3$ and TiTe$_2$ to produce thin films with variable thickness. The exfoliated films were stacked together to form quasi-superlattices. Unlike the epitaxially grown superlattices, the stacked structures are characterized by nearly infinite potential barriers for electrons and phonons. Using the thermal and electrical measure-
ments I have shown that ZT of such structures can be increased over a large temperature range via reduction of the phonon thermal conductivity. It has been previously shown that the core-shell nanostructure-based electrodes enable the combined strength of two or more materials to obtain enhanced energy-power densities in the batteries. The improvement is due to reduction of the Ohmic effects. I investigated the thermal and electrical conductivities of the ultra-long vertically-aligned core-shell carbon nanotubes utilized in the Li-ion battery electrodes. The thermal conductivity, measured with the laser-flash technique, of the carbon nanotubes coated with amorphous silicon and carbon was in the range from 400 to 600 W/mK near room temperature. This is substantially higher than that of the reference battery electrodes. The electrical resistivity was shown to be two orders of magnitude lower than that of the conventional electrode. The results obtained for the Li-ion battery electrodes suggest that the use of nanostructured materials can substantially improve the thermal management of the batteries and their energy storage efficiency.
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Chapter 1

Introduction

1.1 Motivation for Nanostructure-Based Energy Storage and Generation Technologies

The world energy market will demand energy densities of 35.2 trillion kWh by 2035 which is a 31% increase in consumption from 2011 [1]. The United States currently imports 30% of its energy to meet the present electricity demands consumed domestically since domestic consumption exceeds production [2]. To address the energy generation and storage needs, the Department of Energy (DOE), Federal Energy Regulatory Committee (FERC) and National Institute of Standards (NIST) have detailed an energy roadmap to reduce our foreign dependency on energy while increasing the demand of renewable energies [3, 4, 5]. This initiative articulates a national energy portfolio which will increase the production of renewable electric energies from photovoltaic, wind, wood, biofuels and hydroelectrics to create a utility scale energy generation and storage for a smart grid system which will
support a large scale plug-in electric vehicle system. In addition to the current technologies, there are emerging renewable energy resources such as thermoelectric and ocean devices entering the global energy market [6, 7]. The demand for renewable energies will be created by (1) enabling utility systems and private facilities to utilize renewable sources of energy local and through grid distribution, (2) create a large scale electric transportation for the growing plug-in electric vehicles (EV). Since the utility grid distribution varies based on demand while EVs require rechargeable batteries to generate and store the energy based on usage, the need for high performance and long term storage will be required for high power densities to supply electricity to the grid and high energy densities for long term operation of EVs.

There are currently a range of energy generation and storage (e.g lithium-ion rechargeable battery) technologies that currently meet a need for large and small scale deployment for on-grid, EVs and portable electronics [8]. Lithium-ion (Li-ion) batteries hold over 50% of the $20 billion market as a results of the high specific energy and energy densities for use in rechargeable storage batteries. However, these technologies do not sustain the large specific energy-power and energy-power densities required for high performance and long life times needed for EVs [9, 10, 11, 12]. From the growing demand of longer lasting storage devices needed in the electronics industry, Li-ion batteries have attracted attention in the research and development communities. Li-ion electrochemistry is limited by low power densities from the low ion diffusion rate in the electrodes and electrolyte [13]. It has been shown nanostructuring electrodes could meet the higher currents needed to obtain larger power densities with fast discharging and charging with improved specific capacities.
Figure 1.1: Thermoelectric devices architecture for cooling the junction between two dissimilar materials. It is important to note the majority carriers of the current are pumping the heat away from the junction.

in Li-ion batteries [14].

To meet the challenges for advancing this technology, this dissertation will focus on thermal and electrical characterization of nanostructured electrodes for energy storage and generation in Li-ion electrochemical cells and nanostructured thermoelectric materials for energy generation and refrigeration. It is important to note, thermoelectric devices are a multifunctional technology for renewable energy (See figure 1.1 for an example of a thermoelectric device). On one side, when thermoelectricity converts waste heat into electricity, the energy can be stored when the load is attached to an energy storing device. On the
other side, thermoelectric technology can also act as source of heating or refrigeration with an applied external source. In the former case, thermoelectric technology has the potential to improve the quality of life through production of heat in cold environments. In the later case, thermoelectric devices can act as a cooling or refrigeration device [15]. Thermoelectric cooling will have a pivotal role in removing local heating from application specific integrated circuit (ASIC) processors which are a central impetus to the growing electronics industry.

Thermoelectric devices do not have moving parts and can be scaled very small. Highly efficient thermoelectric devices are fundamentally limited in bulk form with thermoelectric figure of merit (ZT) \( \leq 1 \) at 10 percent of Carnot efficiency. The Carnot efficiency is a way to measure the performance of a thermoelectric device to that of a classical energy converting system. The Carnot efficiency is defined as the amount of cooling by the energy input needed to cool. If thermoelectric devices are going to reach wide spread commercial application then a Carnot efficiency of 30% to 40% is needed. This Carnot efficiency requires a ZT > 3 or 4 to be reached [16].
Chapter 2

Background on Energy Generation and Storage Theory

2.1 Thermoelectric Devices For Energy Generation and Electronic Refrigeration

Thermoelectricity can be divided into three basic device applications: (1) cooling, (2) heating and (3) power generation for energy storage (See figure 2.1). In the case of energy generation, the schematic to the left would be designed with an energy storing device in place of the power source which would be represented as a load. The origins of thermoelectricity became known between 1800’s and 1850 [17] and later revised in the 1930 with the knowledge and application of degenerately doped semiconducting material [15] and reborn in the 1990’s through the application of quantum [18] and spatial [19] confinement. Thomas Seebeck discovered the Seebeck effect in PbS and ZnSb 1822 [17]. Seebeck found by applying a
temperature gradient across these two dissimilar materials, placed electrically in series and thermally in parallel, would produce a current. Jean Peltier latter discovered the direction of current across the junction either cooled or heated the junction between two dissimilar materials. Later in 1854 Lord Kelvin derives the mathematical relationship between the two discoveries where he coins the Seebeck and Peltier effect [20] [21].

When Seebeck first performed his experiments, he unknowingly used two dissimilar materials that were semiconducting. Seebeck’s work was not discovered again until the early 1900’s with Ioffe’s [15], director of the Institute for Semiconductors of the U.S.S.R. Academy of Science, investigations where he shows degenerately doped semiconducting materials would produce higher thermoelectric effect than metals would. Ioffe’s reports show thermoelectric performance as a function of carrier concentration. Ioffe demonstrated
that semiconductors for thermoelectrics are optimized when they are degenerately doped. He also introduces the figure of merit, Z, as the ratio of thermoelectric power factor to the thermal conductivity. Ioffe was the first person to demonstrate thermoelectric devices. In the 50’s Goldsmid et al. [22] demonstrates a ZT = 0.0271 in p-type Bi$_2$Te$_3$. Here, the figure of merit, ZT, is defined to compare the intrinsic properties of thermoelectric materials where $T$ is the temperature gradient across the junction. He argued the ratio of thermal to electrical conductivity would be higher in semiconductors than in metals. Due to limits in material technologies, he was only able to demonstrate a thermoelectric junction with (“Bi$_2$Te$_3$ and bismuth”) i.e. semiconductor-metal junction. Later in 1955, Goldsmid et al. demonstrates a ZT for n-type Bi$_2$Te$_3$ [23]. It is important to note, the early reports of the thermoelectric figure of merit was a function of the mean average temperature ($\Delta T$) from the environment with the maximum temperature gradient ($T$) across the junction.

The main challenge was to discover a large figure of merit at a $T = 300 \, \text{K}$. In the first experiments by Goldsmid et al., in 1954 to 1955, he arrived at ZT with $\Delta T = 20 \, ^\circ\text{C}$ and a $T = 33 \, ^\circ\text{C}$.

After 1954, most of the results shows similar reports in ZT with Bi$_2$Te$_3$ p-type and n-type junction at greater $\Delta T$’s. There are two notable report on both n- and p-type Bi$_2$Te$_3$ materials in 1957. One report appeared by Shilliday et al. [24] demonstrating ZT = 0.196 and 0.25 for p- and n-type; respectively. Each leg of the thermoelectric junction was measured at $\Delta T = 65 \, ^\circ\text{C}$ at $T = 49 \, ^\circ\text{C}$. The second report was from a Russian group, Sinani et al. [25, 26], demonstrating a higher ZT = 0.049 in 1957 with 80% Bi$_2$Te$_3$ and 20 % Bi$_2$Se$_3$. The record in this report was that ZT was experimentally determined.
with a $\Delta T = 80^\circ$ that was $60^\circ$ higher than Goldsmid et al. reports. Later Goldsmid et al. [27] reported the highest $ZT = 0.76$ for Bi$_2$Te$_3$ n- and p-type junction in 1958. The limiting factor for the figure of merit not reaching $ZT > 1$ was the lack of equipment available to synthesize high quality single crystal materials which ultimately limited the understanding of specific material optimization. One should note, Goldsmid et al. reports from 1954 to 1958, Bi$_2$Te$_3$ synthesized through direct fusion methods which limited their initial measurements to only p-type Bi$_2$Te$_3$ in 1954. Later in 1955 Goldsmid et al. reports Bi$_2$Te$_3$ n-type synthesis. Moreover, advantages of quantum confinement of charged carrier and spatial confinement of phonon were not recognized until the 1990’s. At that time thermoelectric research experienced a rebirth.

### 2.1.1 Optimization of Thermoelectric Material Systems and Architectures

The thermoelectric figure of merit, $ZT$, is dimensionless and describes a materials intrinsic properties. Superior thermoelectric materials require that $ZT$ be as high as possible. Disalvo et al. [16] states that a $ZT \geq 3$ or 4 is required for solid state cooling to compete with fans and generators. The figure of merit is defined by [20]:

$$ZT = \frac{S^2 \sigma T}{K_{ph} + K_e} \quad (2.1)$$

where $S = \pm (\Delta V / \Delta T)$ is Seebeck coefficient, $\sigma = 1/\rho = ne\mu$ is the electrical conductivity, $T$ is the temperature, $K_{ph}$ is the thermal conductivity due to phonons and $K_e$ is the thermal conductivity due to electrons. The Seebeck coefficient is quantitatively defined based on
semiconductors (See equation 2.2) [6] or metals (See equation 2.3) [28].

\[
S = \frac{8\pi^2 k_B^2}{3e\hbar^2} \cdot m^* \cdot T \cdot \left( \frac{\pi}{3n} \right)^{2/3} 
\]

(2.2)

Where \( k_B \) is Botlzman’s constant, \( h \) is Plank’s constant, \( T \) is absolute temperature, \( m^* \) is the density of states (DOS) effective mass, and \( n \) is the carrier concentration. It is important to note, the inertial effective mass is proportionally related to the DOS effective mass.

\[
S = -\frac{\pi^2 k_B T}{3e} \left[ \frac{\partial \ln \Lambda}{\partial E} + \frac{\partial \ln S}{\partial E} \right]_{E=E_F} 
\]

(2.3)

Here, \( k_B \) is boltzmanns constant, \( T \) is the temperature, \( \Lambda \) is the mean free path of the electron and \( S \) is the Fermi Surface. Since the 1960’s, the optimization of ZT was engineered based on the reduction of the thermal conductivity due to phonons while preserving the electrical conductivity [15]. However, as manufacturing technologies have matured the degrees of freedom for optimizing ZT has advanced significantly.

### 2.2 Thermal Transport in Low Dimensional Material Systems

The ability of materials to conduct heat is determined by materials’ crystalline structure. Thermal conductivity can be quantitatively defined as \( K = K_{ph} + K_e \), where \( K_{ph} \) and \( K_e \) are of the acoustic phonons and electrons, respectively. The dominant contribution to \( K \) is material dependent. In semiconductors, acoustic phonons carry most of the heat, while electrons carry the heat in metals. At room temperature the thermal conduction of silicon is 145 W m\(^{-1}\)K\(^{-1}\), silicon dioxide is between 0.5 - 13 W m\(^{-1}\)K\(^{-1}\) and copper is 398 W m\(^{-1}\)K\(^{-1}\).
2.2.1 Thermal Conductivity: Contributions from Phonons and Electrons

The basics of heat conduction, for a given material system, begins with the Fourier’s Law:

\[
\frac{\dot{Q}}{S} = -K \nabla T. \tag{2.4}
\]

where \( \dot{Q}/S \) is the heat flux per unit area, \( K \) is the coefficient of thermal conductivity for low temperature gradients \( \nabla T \). The negative sign implies heat is flowing from the hot to cold side of a material. The thermal conductivity due to free charged carriers \( K_e \), can be determined by the Wiedemann-Franz law \([29]\):

\[
\frac{K_e}{\sigma} = \frac{\pi^2 k_B^2 T}{3e^2}. \tag{2.5}
\]

Phonon thermal conductivity is defined as \( K_{ph} = \frac{1}{3} C \nu \Lambda \). Where \( K_{ph} \) is the thermal conductivity due to phonons, \( C \) is the specific heat, \( \nu \) is the phonon group velocity and \( \Lambda \) is the mean-free path of the phonon’s defined as a function of the phonon relaxation rate \( \Lambda = \nu \tau \). Here \( \tau \) is the phonon relaxation time. Substituting the phonon relaxation rate into the thermal conductivity expression, \( K_{ph} \) can be written as a function of the phonon frequency:

\[
K_p = \Sigma_j \int C_j(\omega) \nu_j^2(\omega) \tau(\omega) d\omega. \tag{2.6}
\]

Here \( j \) represents the acoustic branches that carry the heat (i.e. two transverse branches and one longitudinal branch) \([30]\) \([31]\).

2.2.2 Thermal Engineering through Spatial Confinement

Most materials structured at the nanometer scale do not conduct heat, as well as the corresponding bulk materials. The thermal transport as one goes from bulk to a strictly
Table 2.1: Mechanisms of Thermal Transport

<table>
<thead>
<tr>
<th>Length Scale</th>
<th>Phonon Dispersion</th>
<th>Dominant Scattering Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L \gg \text{MFP}$</td>
<td>Bulk dispersion</td>
<td>3-phonon Umklapp scattering, point defects</td>
</tr>
<tr>
<td>$\lambda \ll L \leq \text{MFP}$</td>
<td>Bulk dispersion</td>
<td>3-phonon Umklapp scattering, point defects, boundary scattering</td>
</tr>
<tr>
<td>$\lambda \leq L \ll \text{MFP}$</td>
<td>Modified dispersion, many phonon populated</td>
<td>3-phonon Umklapp, point defect, boundary scattering.</td>
</tr>
<tr>
<td>$\lambda &gt; L$</td>
<td>Modified dispersion, few branches populated</td>
<td>Ballistic</td>
</tr>
</tbody>
</table>

2D and 1D system has created increased interest \[32\] \[33\] \[34\] \[35\] \[36\]. As the feature size (e.g. thickness) $L$ decreases, the phonon boundary scattering increases. This leads to the decrease in thermal conductivity since $\Lambda > L$. In extremely small structures the decrease may also come from the changes in the phonon spectrum with the corresponding change in the phonon group velocity. For example, bulk silicon has a thermal conductivity of 145 W m$^{-1}$K$^{-1}$. However, silicon nanowires, at diameters of 20 - 40 nm, drops down to about 13 W m$^{-1}$K \[37\]. This is attributed to the feature size, $L$, being smaller than the phonon mean-free path (MFP) of silicon \[37\]. Table 2.1 summarizes the different cases for the system dimension and phonon-mean free path (MFP) with respect to scattering mechanisms. One can see in table 2.1 how the thermal conductivity can be tuned based on the system dimensions \[38\].

Thermal properties are also tunable through extrinsic effects (i.e. by embedding a thin film in a material within another material) to create boundary conditions. These architectures can be found in superlattice structures for thermoelectric applications. If
one considers a superlattice structure with similar materials, the phonon dispersion can be modified through the formation of minibands which produces mini-Umklapp scattering [39]. Balandin et al. shows theoretically, that one must consider how acoustic phonons change in quantum wells (< 50 nm) for two cases: (1) quantum well is free standing and (2) the quantum well is embedded with the top and bottom layer of materials that are rigid and had significantly different elastic properties. They have shown, for the transport of heat in nanostructures is significantly altered. By embedding a quantum well within a rigid material with different elastic properties would impose boundary conditions that would alter phonon dispersion, group velocity and phonon relaxation rates [19].

2.3 Electrochemical Cells for Energy Storage and Generation

Batteries and fuel cell technology are devices composed of electrochemical cells. When these cells are connected in series or parallel the total voltage or capacity will be increased, respectively. When a battery is connected to a load the voltage is defined by Ohm’s law \( U = IR \). Each electrochemical cell converts free energy from an electrochemical reaction to produce electrical energy [13, 40]. The amount of free energy delivered to the cell is expressed as:

\[
\Delta G = -nFE^0,
\]

Where \( n \) is the number of electrons per moles of a product, \( F \) is Faradays constant, and \( E^0 \) is the standard potential of the reaction [13]. The total capacity of a cell is expressed as the total quantity of electricity involved in the electrochemical reaction based on the amount
of active material in the electrode and weight of the battery [41]:

\[ \text{Cell Specific Capacity} = \frac{1}{C_A + C_C + Q_M}. \] (2.8)

Here \(C_A\) and \(C_C\) are the specific capacities of the anode and cathode, respectively, and \(Q_M\) is the specific mass of the electrolyte, separator, current collector and remaining parts. One should note that the specific capacities are also temperature dependent. Specific capacity is expressed in Ampere-hours (Ah) or its gram equivalent (Ah/g) [13]. This dissertation will focus on secondary batteries that have discharging/charging capabilities (i.e. reversible electrochemical reactions as governed by the Nernst equation [14]). There are primary and reserve batteries [13]. Under discharging conditions, the production of current involves the transfer of electrons by oxidation (See equation 2.9) from a negative electrode, (anode) through a resistive load to a positive electrode (cathode) by reduction (See equation 2.10). An ionic conductor (electrolyte) separating the two electrodes transports the cations from the anode to the cathode (See figure 2.2). Once the ions in the electrolyte diffuse to make contact on the opposite electrode the electrochemical reaction is complete. Since the 40’s, lead-acid, Ni-Cd, Ni-MH, and lithium-ion (Li-ion) with reversible electrochemistry have emerged [13, 42]. An example of redox reactions for discharging/charging a Lithium-ion battery is as follows:

\[ Li_xC_6 \rightleftharpoons C_6 + xLi^+ + xe^-, \] (2.9)

\[ Li_{1-x}CoO_2 + xLi^+ + xe^- \rightleftharpoons LiCoO_2. \] (2.10)

In equation 2.9 and 2.10 the Li-ions are rocked between electrodes through discharging and recharging, respectively. The loss of free energy in these redox reactions drives the
conversion of current at the anode which defines the energy (Wh) and power (W) of the cell. Since the volume and weight of the battery is essential to design higher capacity batteries, the energy and power is normalized by its volume or weight to observe the energy density (Wh/cm$^3$), specific energy (Wh/kg), and power density (W/cm$^3$), and specific power (W/kg) respectively [13]. The specific energy defines how much specific power is consumed over a length of hours used. The specific energy-power can be expressed as [13]:

$$E(t) \frac{kg}{kg} = \bar{U} \int I dt \quad (Wh/kg) \quad (2.11)$$

$$P(t) \frac{kg}{kg} = \bar{U} I(t) \quad (W/kg) \quad (2.12)$$

Here $\bar{U}$ is the average cell voltage, $V$ is the volume of the cell and $I$ is the current produced from the electrochemical reaction. In most cases, batteries are unable to achieve high energy
densities and high power densities [43]. The design of an electrochemical cell is complicated and requires essential rules to achieve high current efficiencies in cell designs and can be found in greater detail in [13, 43]. However, in principle the negative and positive electrode surfaces need to be immersed in the electrolyte that is not electrically conducting to prevent short circuiting. The energy density or power density is defined based on the balance between the anode and cathode material morphology as a tradeoff between high power or high energy. To achieve higher energy-power cells the cathode is selected to find the proper anode to balance the specific performance (See table 2.2\(^1\) and figure 2.4 for cell specific capacity as

\(^1\)Battery University website
Figure 2.4: Is a quantitative description of total cell specific capacity vs. anode specific capacity at various cathode specific capacities (Model after Kasavajjula definition in equation 2.8 [41]). Cathode specific capacities ($C_C$) of 110 mAh/g and 200 mAh/g were modeled after values reported by Kim et al. [44] and Lee et al. [45] respectively. The weight of the remaining cell elements is assumed 130.4 mAh/g [41] to show a basic comparison of varying electrode specific capacities.

a function on electrode specific capacity). During the operation of these cells, they are limited to polarization effects occurring during discharging/charging which create waste heat. Since polarization is part of the driving mechanism for energy conversion, waste heat is unavoidable. Therefore is it critical to have electrodes which have intrinsically high thermal conductivity and low resistivity to increase the current conversion efficiencies [46]. Fur-
Table 2.2: Energy vs Power Density Tradeoffs for Li-ion Cathodes

<table>
<thead>
<tr>
<th>Energy vs Power Density</th>
<th>Cathode(s)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Power Density</td>
<td>LiMn$_2$O$_4$</td>
<td>Power Tools</td>
</tr>
<tr>
<td></td>
<td>LiFePO$_4$</td>
<td>Power Tools</td>
</tr>
<tr>
<td></td>
<td>LiNiMnCoO$_2$</td>
<td>Power Tools</td>
</tr>
<tr>
<td>High Energy Density</td>
<td>LiNiO$_2$</td>
<td>Portable Electronics</td>
</tr>
<tr>
<td></td>
<td>LiV$_3$O$_8$ [47]</td>
<td>Portable Electronics</td>
</tr>
<tr>
<td></td>
<td>Li$_x$TiS$_2$ [48]</td>
<td>Portable Electronics</td>
</tr>
</tbody>
</table>

Furthermore, accurate management of the thermal conductivity in electrodes will help reduce the temperature variations which affect the ionic diffusion through the electrolyte, current conversion, energy, power, cell voltage, rate discharge/charging currents, cycle ability, cell lifetime and overall performance [13]. There are three types of polarization effects that lower the cell voltage: (1) activation polarization, (2) concentration polarization and (3) Ohmic polarization. Activation polarization occurs at the electrode surface which controls the electrochemical reaction. Concentration polarization results from difference in concentration with redox reactions (i.e. differences in reactant and products). Ohmic polarization occurs from resistivity of the electrode and the amount of current being produced from the redox reaction. These polarization losses can be expressed in voltage [13]:

$$U = U_o - [(\eta_{ct})_a + (\eta_c)_a] - [(\eta_{ct})_c + (\eta_c)_c] - iR_i = iR$$  \hspace{1cm} (2.13)$$

Here $U$ is the operating voltage, $U_o$ is the open circuit voltage, $(\eta_{ct})_a$ and $(\eta_{ct})_c$ are the charge-transfer overvoltage at the anode and cathode, $(\eta_c)_a$ and $(\eta_c)_c$ are the concentration polarization at the anode and cathode, $i$ is the load current, $R_i$ is the internal resistance of the cell, and $R$ is the resistance of the cell on a load. Overvoltages are the over discharging
or over charging that effect the negative and positive electrode, respectively. Recently, due to the development of portable electronics demands for longer battery life and electric vehicle charging needs, high energy densities and/or fast discharging/charging properties are becoming increasingly important [9, 49].
Chapter 3

Thermoelectric Performance of Nanostructured Bi$_2$Te$_3$ Layers

3.1 Mechanically Stacked Bi$_2$Te$_3$ Quasi-Superlattice

The main challenge in the thermoelectric industry was the inability to achieve $\text{ZT} > 1$ with bulk materials. Conventional materials used in the industry are divided in low, mid and high temperature ranges for materials including Bi$_2$Te$_3$ and its alloys, PbTe and SiGe; respectively. As a result of the material size, weight and ZT performance, these conventional materials do not have the ability to efficiently pump the charged carriers either away or towards the junction. The pumping action in a material is defined as follows [50]:

$$q_{\text{max}} = \frac{1}{l} \left[ (0.5S^2\sigma T_{\text{cold-side}}^2) - K(T_{\text{hot-side}} - T_{\text{cold-side}}) \right]$$

(3.1)

where $l$ is the thickness of the thermoelectric material, $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $K$ the thermal conductivity and $T$ the temperature. This equation
shows a materials ability to pump heat from one side of a thermoelectric junction to another. To achieve a state-of-the-art thermoelectric material, $q_{\text{max}}$ needs to larger than 500 Wcm$^{-2}$ with a thickness $l < 50 \mu$m. The pumping efficiency, $q_{\text{max}}$, directly through (1) achieving the highest electrical power factor, $S^2\sigma$, and (2) creating a material with the smallest possible thickness.

The reports over the last two decades identified both theoretical and experimental studies demonstrating a $ZT \geq 1$ can be achieved through quantum confinement of the charged carrier and spatial confinement of phonon’s. The experimental research using MBE has proven thermoelectric materials can be synthesized $< 50 \mu$m. This new development in using nano-materials, e.g thin films, has enabled quasi-2D and quasi-1D confinement thermoelectric material.

Early in the 1990’s there were theoretical reports that justified a new trend in thermoelectric research. These data suggested two new ways to engineer thermoelectric materials: (1) $ZT$ enhancement could be increased by creating superlattice structures of well widths approaching the atomic scale ($< 50$ nm) and (2) increasing $ZT$ by spatially confined phonons through boundary scattering in well width $< 150$ nm. In 1993, Dresselhaus et al. [51, 18, 52, 53] theoretically observed the enhancement of $ZT$ over varying well width for quasi-2D [51] and quasi-1D [53] superlattice structures. These predictions showed $ZT > 2$ can be achieved through quantumly-confined systems e.g. quantum well $< 100$ nm height and quantum wires $< 100$ nm in diameter [51]. Where a quantumly confined system can be understood as the spatial confinement of a charged carrier in either one or two directions. Balandin et al. [54] proposed a new area in thermoelectrics known as phonon engineering.

20
where a phonon is defined as a quanta of lattice vibrations. Phonon engineering considers strong modification of the phonon group velocities due to spatial confinement of phonons resulting in significant increase of phonon relaxation rates, thus, a considerable drop in lattice thermal conductivity in a quantum well [19, 55]. To accomplish this, proper tuning of the size, shape, interface and mass density of the nanostructures can change the phonon spectrum in a desired way. Furthermore, in 1995 Broido and Reinecke [56] considered how a thermoelectric superlattice thermoelectric figure of merit, $ZT$, could be achieved in a practical system. They theoretically showed how $ZT$ can be increased in a superlattice by (1) considering the thermal conductivity of the buffer layer relative to the quantum well and (2) the electron tunneling that occurs when superlattice periods are small. They showed ZT as a function of superlattice well widths for several potential barriers barrier heights. They argued the mechanism to this enhancement is due to the fact that the potential barrier heights are proportional to a materials density of states.

3.1.1 Motivation for Superlattice Quantum Structures

Superlattice structures offer improved performance for carrier transport parallel or orthogonal to the growth axis. The mechanism of carrier transport parallel to the growth axis, i.e. perpendicular transport, is the miniband formation from the superlattice period. Additionally, superlattices can engineered for a phonon-blocking/electron-transmitting regime which significantly reduces the cross plane thermal conductivity and while enhancing the free carrier transport. Superlattice structures contain two materials in an alternating sequence being stacked along the z-axis to form a quasi-superlattice. Consider a superlattice
quantum structure with material A at a thickness of $L_A$ and material B at a thickness $L_B$. The periodic repeating unit of the superlattice is $D$, where $D = L_A + L_B$. Superlattice structures have fixed well width along the growth direction where the thickness of the quantum well (QW) is defined by the thickness of material A, $L_A$, and the distance between the neighboring QW is $L_B$; the buffer layer thickness. The solid state physics of the material governs the quasi-2D intrinsic and extrinsic confinement within this quantum structure e.g. quantum confinement of electrons, DOS, confining potential and elastic properties. Fundamentally, material A is considered embedded within material B where the bandgap of material A has a bandgap smaller than material B. This creates partial/full confinement of the free carriers within material A.

In realistic superlattice structures, the performance is limited by the material quality and confining potential. This leads to superlattice quantum structures with finite quantum wells. The ideal superlattice would have fixed wells widths, $L_A$, with infinite potential barriers [57]. Where the infinite potential barriers achieves full quantum confinement of the electron wave function (i.e. the electron wave function would not have a decaying term in the neighboring buffer layer). The confinement of the free carriers are dependent on the bandgap, i.e. potential barrier created by material B [56], and the thickness of that layer [58]. Broido and Reinecke [56] showed the potential barrier can greatly effect the full or partial confinement of the wave function within quantum well. If the wave function of free carriers decays into the adjacent well, the electronic transport will be perturbed and reduced. However, if the potential barrier increases in the quantum well, the confining potential increases and decaying wave function will have less of a decay into the adjacent
quantum well while increasing the quasi-2D DOS. The confinement of the wave function can be quantitatively understood through the confining energy $\epsilon_n$ in a finite potential quantum well (See equation 3.2 and Ref [58] for the explicit derivation of confining energy in a finite potential well embedded with another material).

$$\epsilon_n = \frac{\hbar^2 k^2}{2m^*_A} - V_o,$$  

(3.2)

where $\hbar$ is planks constant, $k$ is the wavevector, $m_A^*$ is the effective mass of the carriers in material A and $V_o$ is the potential. Broido and Reinecke [56] predicted the greatest advantage of carrier confinement to occur in the case when a potential barrier is large e.g. quantum well embedded within an electrically insulating material. Due to limitation in growth technologies in chemical vapor deposition (CVD), molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD) and electrochemical depositions and intrinsic material properties, infinite potential barriers are difficult to achieve in realistic quantum structures. When material A and material B are selected, the full confinement of the carriers can be improved by: (1) selecting the proper thickness of the confining layer, material A, while increasing the thickness of material B to reduce the amount of overlapping wave functions decaying from the neighboring A layer. This architecture is challenging since the DOS in a quantum well superlattice needs to be has high as high as possible.

### 3.1.2 Significance of Bi$_2$Te$_3$ Material Systems and Structures

State-of-the-art thermoelectric materials are optimized via the quantum confinement of free carriers [51, 18, 52] and spatial confinement of phonons [54, 59]. Due to the advancements of manufacturing materials, thermoelectric devices can be designed with quantum structures
superlattices), that create 2D, quasi-2D, 1D and quasi-1D confinement effects. This enables new possibilities for tuning parameters such as: (1) increasing the density of state (DOS) and (2) improving electronic transport. By increasing the DOS closer to the Fermi energy, the Seebeck coefficient will be larger since the DOS mass is proportional to the inertial mass [6]. Experimentally, the DOS can be increased by reducing the volume or height scale of the quantum well. The balance between the Seebeck, DOS energy and effective mass is complex, however, since the effective mass is bandgap dependent and can be increased with flat narrow bands [6]. In the later case, the electronic transport can be designed based on the superlattices. The quantum structure allows enhanced transport either in-plane or cross-plane based on the material band structure and buffer layers. In-plane transport will be enhanced based on full confinement of the charge carriers while cross-plane transport will be enhanced based on miniband formation.

Recent advances in manufacturing technologies for material research and development have enabled ultra-thin film development. Now experimental research in quasi-2D and quasi-1D crystalline films utilizing quantum confinement of charged carriers in thermoelectric quantum structures are key to the recent major advances in $ZT > 1$ (See figure 3.5). With the emergence of thin film materials synthesis, bandgap engineering enables higher $ZT$ values in semiconducting materials and metals can go under a metal-to-semiconducting transition at ultra-small height scales [18]. Dresselhaus et al. [18] demonstrates bismuth, with metallic properties, in a quasi-1D geometry can achieve a $ZT > 2$. However, the enhancement of $ZT$, for a semiconductor or a metal, is fundamentally limited by conflicting properties (e.g., Seebeck coefficient and thermal properties). The optimization of
Figure 3.1: These are the current data of both experimental and theoretical reports for n- and p-type materials. These reports include 1D and 2D structures and superlattice quantum structures for a range of materials for both either one leg of a thermoelectric device or a junction. It is important to note, this data is for a wide temperature range of reports.

the large thermopower $|S|$, high electrical conductivity and low thermal conductivity is engineered through quantum confinement of charged carriers and spatial confinement of phonons in superlattice structures. The carrier mobility and Seebeck coefficient are interrelated through carrier concentration \([15]\) and can be expressed through parabolic band and energy-independent scattering approximation \([6, 21]\) (See equation 2.2). For example in a semiconductor, low carrier concentrations achieves a high Seebeck coefficient \([15]\) which
creates lower electrical conductivity. Where the Seebeck coefficient and electrical conductivity \((\sigma)\) are interrelated by \(n\) (See equation 2.2). The Seebeck coefficient and electrical conductivity defines the electrical power factor \((S^2\sigma)\) which is optimized at carrier concentration of \(10^{19}\text{cm}^{-3}\). The benefit of degenerately doped semiconductors enables the charged carriers to propagate the heat through the lattice.

### 3.2 State-of-the-Art Thermoelectric Materials

In the 1990’s, MBE had been developed by Bell Labs for about 30 years. The first theoretical Thermoelectric predictions were published by Hicks and Dresselhaus [52, 53] at Massachusetts Institute of Technology (MIT) which renewed the interest in thermoelectric engineering. Sales et al. [60] at Oak Ridge National Laboratory and Harman et al. [61] from MIT synthesized thin film superlattice produces exceptional results. Sales et al. [60] manufactured bulk \(\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}\) material in an evacuated silica tube within a furnace [60] to report a measured \(ZT = 1\). Harman et al. [61] found that MBE grown \(\text{Pb}_{1-x}\text{Eu}_x\text{Te}/\text{PbTe}\) is a promising thermoelectric material. The motivation of the design is to increase the density of states per unit volume in superlattices architecture where PbTe quantum wells are embedded around \(\text{Pb}_{1-x}\text{Eu}_x\text{Te}\). PbTe well widths are 4.5 to 6 \(\mu\text{m}\) and \(\text{Pb}_{1-x}\text{Eu}_x\text{Te}\) buffer layer thicknesses in the range of 110 to 190 nm with approximately 120 periods [61]. This new material is reported to have a \(ZT > 1.2\) in 1997. Venkatasubramanian et al. [62] developed a method to synthesize \(\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3\) superlattices with 1 and 8 nm periods. Balandin et al. [19, 54] released two papers that described the increase in \(ZT\) in a superlattice through spatial confinement of bulk phonons and confined phonon as quantum well widths approach
1 nm. The mechanism for increasing ZT in ultra-thin quantum wells is the modification of the phonon group velocity due to the confinement of the acoustic phonon modes, which leads to the reduced thermal conductivity of the superlattice [63, 54, 59].

In the recent years a large part of academic research in thermoelectrics has included MBE, MOCVD and electrochemical deposition where ultra-thin materials are investigated for their quasi 2D and quasi-1D enhancement. In 2001 Venkatasubramanian et al. [62] reports a ZT > 2 for Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices at 1 nm and 5 nm respectively. Further demonstrating thermoelectric devices could be made small enough to specifically act as a cooling mechanism for local hot spots on a processor. Beyer et al. [64] and Harman et al. [65] released reports of ZT = 1.2 and ZT > 1.6; respectively. Beyer developed MBE grown PbTe/PbSe$_{0.2}$Te$_{0.08}$ for parallel transport to the layer planes. The PbTe well widths were < 1 nm and PbSe$_{0.2}$Te$_{0.08}$ buffer layers thickness of 1.8 nm [64]. Harman reports quantum dots superlattices with PbSeTe/PbTe quantum dots and claims this material architecture to perform better than (Bi,Sb)$_2$(Se,Te)$_3$. Current low dimensional materials, since the year 2004, include quasi-2D silicon nanoribbons [66] and quasi-1D wires [67], Bi$_2$Te$_{3-y}$Se$_y$ nanowires at varying diameters [68], non-aligned arrays of nanowires BiSbTe [69], and nanocomposites of varying diameters [70, 71].

### 3.3 Thermoelectric Characteristics of Bi$_2$Te$_3$ Quasi-Superlattices

Transport measurements have been performed on a bulk Bi-Te ingot and Bi-Te quasi-superlattice [57] samples and compared to commercially available p-type Bi-Sb-Te. The term Bi-Te is used since each sample stoichiometry varies. The Bi-Te quasi-superlattice
samples are multilayers with a non-periodic well structures, where the layers of Bi-Te were fabricated by graphene-like exfoliation [57]. The exfoliated films were re-stacked on each other to form as a quasi-superlattice [57]. The quasi-superlattice is characterized by strong confinement of electrons and phonons.

The transport data are extracted from the van der Pauw and Hall measurements over a wide temperature range. The thermoelectric characteristics extracted from the Hall measurements included the resistivity, Hall coefficient, majority carrier concentration, mobility, and sheet resistance enabled the extraction of conducting properties (e.g. metallic or semiconducting) and ideal operating performance as compared to bulk. The cross-plane thermal properties is extracted by a laser flash technique. Details of the instrument setup can be found in the preceding chapter (See figure 5.4).

3.3.1 Thermoelectric Characterization of Bi$_2$Te$_3$ Quasi-Superlattices

The Bi-Te family of materials are known low-temperature and room-temperature thermoelectric materials [72]. The thermoelectric characteristics of the quasi-superlattices films were measured at temperatures between 150 K and 450 K. In the case of the Bi-Te quasi-superlattice sample, it is important to understand how the exfoliation effects the resistivity, carrier concentrations, and conductive properties across this wide temperature range. Figure 3.2 demonstrates the measured results for the quasi-superlattice, ingot and bulk Bi-Te and compared to that of a p-type Bi-Sb-Te commercial sample. One should note, our stoichiometry analysis of the atomic compositions from X-ray EDS scans has been indicated in figure 3.3.
Figure 3.2: On the top left is the resistivity over a wide temperature range to establish the transport behavior for the Bi-Te quasi-superlattice and ingot Bi-Te samples. These samples are also compared to standard bulk samples for comparison. The top right figure shows the measured Hall coefficients over a wide temperature range. Here the Bi-Te quasi-superlattice film indicate p-type conduction. Where the ingot sample appears to change conduction type at lower temperatures. Mobility is shown on the bottom left figure and compared to another p-type material. The thermal conductivity and specific heat is measured for the ingot sample in the bottom right.

Both the ingot and quasi-superlattice samples indicated p-type properties with an atomic percent of tellurium below 59.5% [73]. Additionally, the ingot Bi-Te resistivity measurements indicate semiconducting properties through a non-linear behavior with temperature. The quasi-superlattice Bi-Te samples, however, demonstrates a clear monotonic dependance with temperature. It is possible the stated sample is still p-type as measured by the X-ray EDS although the in-plane resistivity data reveals metallic transport. Since
the quasi-superlattice Bi-Te film has atomically thin quantum wells of Bi-Te, the extracted electrical data is complex [74, 75, 76]. Further analysis is needed to determine the nature of the in-plane conductive properties of the Bi-Te quasi-superlattice samples.

3.3.2 Thermal Conductivity of Bi$_2$Te$_3$ Materials and Structures

Thermal conductivity of the bulk Bi-Te ingot sample has been investigated using a laser flash based technique (See figure 5.5) and the thermal conductivity of the Bi-Te quasi-superlattice has been investigated by Goyal et al. [57]. The thermal conductivity $K$ is related to $\alpha$ as $K = \alpha \rho C_p$, where $\rho$ and $C_p$ are the density and specific heat of the material, respectively. Details of the experimental setup and measurement procedures were reported by us elsewhere [77, 78, 79]. The system used for this study was calibrated with other techniques for measuring thermal conductivity such as transient planar source and 3-omega techniques [79, 80, 81]. Based on the experimental procedure, information about the material must initially be addressed. The density of the material ($\rho$) is assumed to be the same as conventional Bi-Te bulk materials based on the energy dispersive spectroscopy (EDS) (See figure 3.3). Where the EDS spectrum identified a 13% deviation from the Bi$_2$Te$_3$ crystal structure (See table 3.1). Bismuth tellurium as been a well studied for over 100 years in bulk form is well known and the doping concentration through tellurium deviation as been shown [73]. Based on known tellurium deviation, the conduction type is assumed p-type (See table 3.1).

To ensure proper experimental measurement of the thermal conductivity, the specific heat $C_p$ needed to be calculated. The specific heat can be extracted from the laser flash
Figure 3.3: EDS spectrum of the Bi-Te quasi-superlattice and ingot sample. The stoichiometric percentages demonstrate a p-type material for the concentration of tellurium in the Bi-Te quasi-superlattice and Ingot sample. It is important to note the quasi-superlattice detected Zn and Al as indicated by the blue arrows.

The laser flash technique by comparing the temperature rise of a known sample with a temperature rise of an unknown sample. Since the laser flash technique measures the transient voltage response and not a transient temperature response, a calibration is done based on the experimental parameters of each sample. Under small temperature rises, the change in temperature, $\Delta T$, is proportional to the ratio of change in voltage $\Delta V$ to the amplifier gain, $G$. Where the

Table 3.1: Bi-Te Conduction Type Based on Tellurium Concentration

<table>
<thead>
<tr>
<th>Bi-Te Material</th>
<th>Tellurium At%</th>
<th>Formula</th>
<th>Carrier Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quasi-S.L.</td>
<td>52.49</td>
<td>Bi$<em>2$Te$</em>{2.21}$</td>
<td>holes</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>56.51</td>
<td>Bi$<em>2$Te$</em>{2.59}$</td>
<td>holes</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>59.5</td>
<td>Bi$<em>2$Te$</em>{2.94}$</td>
<td>holes</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Bi$_2$Te$_3$</td>
<td>holes</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>60.5</td>
<td>Bi$<em>2$Te$</em>{3.06}$</td>
<td>electrons</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>Bi$<em>2$Te$</em>{3.13}$</td>
<td>electrons</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>61.5</td>
<td>Bi$<em>2$Te$</em>{3.19}$</td>
<td>electrons</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>Bi$<em>2$Te$</em>{3.33}$</td>
<td>electrons</td>
<td>[73]</td>
</tr>
</tbody>
</table>
amplifier gain is an established when setting the light pulse (See equation 3.3):

\[
\Delta T \propto \frac{\Delta V}{G_{\text{ampl.gain}}} 
\]  

(3.3)

The reference sample, for this study, was a pyroceram material with a thermal conductivity of 4 W/mK at room-temperature. This value is based on the measured data from our laser flash technique. The measured specific heat follows techniques reported by Parker [83]:

\[
Q = \text{absorbed energy} = (mC_p\Delta T)_{\text{ref}} = (mC_p\Delta T)_{\text{sample}} 
\]  

(3.4)

Here \( m \) is the mass of the material and can be calculated from the volume and density of the sample, \( C_p \) is the specific heat, \( \Delta T \) is the temperature rise. The measured specific heat is shown in figure 3.2. A Cowan [84] thermal model was used to fit the transient voltage response with sample thickness to identify the thermal diffusivity. The temperature dependent thermal conductivity is shown in 3.2. The weak temperature dependance of the Bi-Te ingot sample does not have a \( 1/T \) dependance and can be consider a disordered crystal. This results in the high thermal conductivities which is not characteristics of highly crystalline Bi-Te samples [27].

### 3.3.3 Thermoelectric Figure of Merit of Bi\(_2\)Te\(_3\) Quasi-Superlattices

The thermoelectric figure of merit over a wide temperature range is shown for the quasi-superlattice and ingot sample. We have demonstrated the quasi-superlattice at room temperature is 77\% enhanced from the ingot sample (See figure 3.5). The quasi-superlattice also shows similar enhancement of the entire temperature range of 150 K to 300 K. Bulk Seebeck value was assume from Ref [85] for both the quasi-superlattice and ingot samples.
Figure 3.4: The thermoelectric figure of merit for a Bi-Te quasi-superlattice and ingot sample. Here a 77% increase is found with the Bi-Te quasi-superlattice sample. It is clear that the reduction in lattice thermal conductivity is enhanced by the performance of the thermoelectric characteristics.

However, further investigation is needed for the Seebeck results for the quasi-superlattice as compared to the bulk values. The quasi-superlattices at room-temperature showed reasonable agreement with the currently reported ZT values of state-of-the-art thermoelectric materials (See figure 3.5).
Figure 3.5: State-of-the-art data of experimental reports for the figure of merit for n- and p-type Bi$_2$Te$_2$ materials at room temperature. These reports include 1D and 2D structures and superlattice quantum structures for one or both legs of a junction. Our ZT value of mechanically exfoliated Bi-Te quasi-superlattice matches the current ZT trend.
Chapter 4

Quasi 2D Titanium Telluride Crystals for Thermoelectric Applications

4.1 Mechanically Exfoliated Quasi 2D Crystals

The discovery of graphene’s (i.e. a single atomic plane of carbon atoms) unique electrical \[86\] and thermal properties \[87\] stimulated a strong interest in atomically thin films (< 5 nm), which can be obtained by a graphene-like mechanical exfoliation process. This interest is driven by the possibility of obtaining new electronic and phonon properties and functionality in the ultra-low dimension crystalline thin films. These atomically thin films, i.e. ultra low-dimensional films, are subjected to significantly different properties and functionality from their bulk source. In the case of a perfect crystalline bulk material system, charged carriers
Table 4.1: Tuning Parameters for Electrons and Phonons

<table>
<thead>
<tr>
<th>Tuning Parameter</th>
<th>Electrons</th>
<th>Phonons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waves</td>
<td>( E_G ) of constituents</td>
<td>( \zeta = \rho V_s )</td>
</tr>
<tr>
<td>Governing Equation</td>
<td>( \Psi ) electron de Broglie wave</td>
<td>( u ) vibrational or sound waves</td>
</tr>
<tr>
<td>Bulk Limit</td>
<td>Schrodinger</td>
<td>Elastic Continuum.</td>
</tr>
<tr>
<td></td>
<td>( E = \frac{\hbar^2 k^2}{2m} )</td>
<td>( \omega = c, k )</td>
</tr>
</tbody>
</table>

Electrons and Phonons can move along \( x, y \) and \( z \) directions and the phonons are not spatially confined. In a strictly 2D case, charged carriers can move only in the two directions orthogonal to the direction of growth, where motion in the third direction is confined to a well defined portion of space by momentum, energy and wave-function quantization. The quasi-2D means the \( z \)-direction is defined by one or few energy levels and the phonons are spatially confined as a result of the height scale and material boundary conditions relative to the materials phonon MFP. This case happens only in atomically thin structures and/or at low temperatures [58]. In a 2D and quasi-2D regime the charged carriers and phonons are said to be in a quantumly confined regime. The following table 4.1 summarizes the mechanisms for tuning charge carriers and phonons.

Experimentally, quantum confinement of exfoliated flakes can be detected optically, in a material when light penetrates the known absorption depth. In the case of exfoliated graphene atop of Si/SiO\(_2\), with an oxide thickness of 300 nm, a purplish tint is observed [88]. This same observation is shown in hexagonal Boron Nitride [89]. Since the absorption depth is material dependent, the height scale (well width) for quasi-2D confinement will vary according to the quantum regime of that system. Typically these effects can be visually identified optically through a microscope. Additionally, Raman spectroscopy has
Figure 4.1: Graphene-like exfoliation process for any layered material using scotch tape. Note here the silicon dioxide layer has a specific thickness of 300 nm, the silicon is heavily doped to act as a metal for use as a back-gate, and the gold layer is used to make contact to the silicon substrate for back-gating.

also been described as a robust technique used to identify specific height scales of materials (i.e. nanometrology) [90] [91].

As materials are thinned from their bulk form to their monolayer i.e. single atomic sheets, we can expect to reach the maximum two-dimensional quantum confinement. This can lead to potential changes in the electrical conductivity [88, 92], thermal conductivity [19, 54, 93, 94] and electronic structure [95] modification of materials. We have employed a new process and methodology known as graphene-like mechanical exfoliation to study new quasi-2D materials. Graphene-like exfoliation uses materials with a layered structure, "scotch tape", and a Si/SiO$_2$ substrate where the oxide is tuned to enable optical visibility under white light or filtered conditions [96]. The layered material is placed between two pieces of the tape and then peeled in an iterative process. This allows one to isolate the materials mono-layers by taking advantage of the van der Waals gap between consecutive layers along the c-axis. Second, the tape is then placed atop of Si/SiO$_2$ substrate with an oxide thickness of 300 nm. This process is then repeated many times (See figure 4.1).

Novoselov and Geim et al. [97] demonstrated exfoliation of NbSe$_2$, MoS$_2$, BN, and
Bi$_2$Sr$_2$CaCu$_2$O$_x$ in a method similar to graphene’s exfoliation. Further research with MoS$_2$
lead Mak et al. [98, 99] to discover that MoS$_2$ bandgap crosses over from an indirect bandgap, in bulk, to a direct band gap in single layer form [95]. Since this discovery, mechanically exfoliated MoS$_2$, has been studied in great detail. Contrary to the success of mechanically exfoliated layered materials via the mechanical exfoliation there have been few reports, to-date, of new layered material systems produced by mechanical exfoliation. One of the few studies of new layered materials systems is bismuth telluride (Bi$_2$Te$_3$). Teweldebrhan et al. [74] experimentally investigated a known thermoelectric material ("Bi$_2$Te$_3" ") could also be subjected to graphene-like exfoliation. They experimentally demonstrated quasi-2D crystals of ("Bi$_2$Te$_3" "), known as a quintuple with five atomic planes separated by the van der Waals gaps [100] could be exfoliated.

4.1.1 Motivations for Investigation of Ultra-Thin TiTe$_2$ Crystals

Titanium Telluride (TiTe$_2$) has been investigated as a possible low-temperature thermoelectric material with the charge-density wave (CDW) transitions below 150 K in bulk form [101, 102, 103]. The metallic behavior of titanium telluride makes this material a non-conventional thermoelectric material, however, recent reports show metal to semiconductor transitions occur in bismuth (Bi) through quantum confinement [18] and CDW materials exhibiting a ZT > 1 in high temperature phase transitions [104]. Dresselhaus et al. [18] demonstrates overlapping valence and conduction bands in bulk bismuth can be altered to induce a bandgap by quantum confinement in 100 nm diameter wire of Bi. Dresselhaus et al. observes this confinement effect can increase ZT ≥ 2. Rhyee’s et al. [104] shows In$_4$Se$_3$
bulk structure has quasi-1D chains of In$_4$Se$_3$ that have CDW phase-transitions. Their investigation reported a $\text{ZT} = 1.49$ at 700 K. Furthermore, recent advances in low temperature growth processes [105, 106] have shown a need to use atomically thin TiTe$_2$ as a method to remove inter-diffusion of layers between ultra thin quantum wells and buffer layers in Bi$_2$Te$_3$ architectures. A superlattice grown by modulated elemental reactants (MER) is motivated by low temperature growth process $< 500 ^\circ\text{C}$. Structures such as $((\text{Bi}_2\text{Te}_3)_x(\text{TiTe}_2)_y)$ and $((\text{TiTe}_2)_3(\text{Bi}_2\text{Te}_3)(\text{TiTe}_2)_3(\text{Sb}_2\text{Te}_3)_2)$ have been investigated with the incorporation of TiTe$_2$ into Bi$_2$Te$_3$ based thermoelectric quantum structures [107, 108, 109, 92]. However, to-date, only thermal investigations [92] have been reported in thin films of TiTe$_2$ while the electrical properties of atomically thin films of TiTe$_2$ and the superlattice have not yet been reported.

4.1.2 Quasi-2D Titanium Telluride Crystals for Direct Energy Conversion

The electrical properties needed to accurately understand the impact on the thermoelectric characteristics of quasi-2D TiTe$_2$ films still need to be addressed. I report a proof-of-concept method for obtaining atomically thin layers of graphene-like exfoliated titanium ditelluride (TiTe$_2$) [110] and describe the current-voltage properties of the resulting quasi-2D crystals and demonstrate a gating effect through a back-gated field effect transistor device [110, 82]. The presence of the van der Waals gaps enabled the disassembly of TiTe$_2$ crystals into its trilayer building blocks of three monatomic sheets consisting of Te Ti Te and resulting tri-layer derivatives. By altering the thickness and sequence of atomic planes, we were able
to create designer nonstoichiometric quasi-2D crystalline films, tune the Fermi level, and control the type of charge carriers across the channel while inducing a room temperature charge density wave effect. The exfoliated trilayers and ultrathin films have low thermal conductivity, anisotropic electrical conductivity and tunable charge density wave features. We have constructed MOSFET-like structures using quasi-two dimensional crystals of TiTe$_2$ as the channel. Our approach enables a new route to tune the electronic and phonon transport properties of atomically thin thermoelectric and charge density wave materials.

4.2 State-of-the-Art Titanium Telluride Materials

TiTe$_2$ exist in a group of about 40 layered transition metal dichalcogenides which have been extensively studied and compared both optically and electrically since the 60’s [111]. TiTe$_2$ exists in the IVb group within the titanium family of TiX$_2$ (X: S, Se, Te). The family of materials has attracted extensive research as a result of the electronic structure as a semi-metal [112, 113]. Here I review extensively TiTe$_2$, however, a complementary extensive review of the TiX$_2$ (X: S, Se) family of materials can be found in [114]. TiTe$_2$ has been extensively study as a result CDW behavior [112, 101, 102, 103], electronic structure [114, 115, 116, 117, 118], and stable reference Fermi liquid system [119, 120]. Table 4.2 summarizes the experimentally observed resistivity in bulk TiTe$_2$ that have been used to measure the purity and quality of the synthesized TiTe$_2$ material. Quasi-2D [107, 108, 109] and Quasi-1D [121] structures of TiTe$_2$ have been synthesized.

It is known that MX$_2$ materials have CDW transitions which can be identified through 2D Anderson localization in the commensurate phase [123]. Koike et al. [112]
reports TiTe$_2$ does not have CDW phase transitions even though 2D Anderson localization is present. These measurements are reported to have obtained CVD grown stoichiometric powders of TiTe$_2$. The powders are then manufactured into single crystals by placing the powder within an ampule with a temperature gradient [112]. The authors argued TiTe$_2$ is a material system with 2D electrons and 3D holes carriers where the 2D electrons exist at temperatures below 5 K. The authors results where established through comparison of resistivity vs. temperature (0.5 to 300 K), magnetoresistance and Hall effect with J$_\perp$H$_\parallel$c-axis. From these measurements, they concluded that 2D Anderson localization in TiTe$_2$ is not due to CDW behavior. More interestingly they display Hall coefficient verse temperature which shows hole-like carriers below 5 K with a carrier concentration of $10^{22}\text{cm}^{-3}$ and Hall mobility of 25 cm$^2$/V-s.

Boer’s et al. [101] data compares the optical data extracted from angular-resolved ultraviolet photoelectron spectra (ARUPES) and compares them to band structure calculations using augmented plane-wave (APW) method on a polycrystalline sample of Ti$_{1.01}$Te$_2$. The material was prepared first form a powder sample at 750 °C and then forming poly-

### Table 4.2: Resistivity of TiTe$_2$ at Room Temperature

<table>
<thead>
<tr>
<th>Author</th>
<th>Ref</th>
<th>$\rho_{//}(300K)$ $\mu\Omega$-cm</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boer et al.</td>
<td>[101]</td>
<td>145</td>
<td>Exp., polycrystalline, excess Ti</td>
</tr>
<tr>
<td>Koike et al.</td>
<td>[112]</td>
<td>105</td>
<td>Exp., single crystal, bulk</td>
</tr>
<tr>
<td>Allen et al.</td>
<td>[103]</td>
<td>500</td>
<td>Thry based on ARPES results</td>
</tr>
<tr>
<td>Peretti et al.</td>
<td>[120]</td>
<td>95 - 110</td>
<td>Exp., single crystals, bulk</td>
</tr>
<tr>
<td>Chiritescu et al.</td>
<td>[92]</td>
<td>217-243</td>
<td>Exp., misfit layer TiTe$_2$, bi-layer</td>
</tr>
<tr>
<td>Khan et al.</td>
<td>[122]</td>
<td>690 - 2015</td>
<td>Exp., single crystal, excess Te, 100 nm exfoliated thin film</td>
</tr>
</tbody>
</table>
crystalline samples through Iodine-vapor transport. Boer’s et al. [101] concludes the transport data is consistent with band-structure calculations. Boer’s et al. [101] finds Koike’s et al. [112] data regarding resistivity, 3D holes and 2D electrons where the 2D electrons would undergo 2D Anderson localization in good agreement with their results [112]. Boer’s et al. [101] does point out the single crystal samples (single crystal TiTe$_2$) of Koike’s et al. [112] are closer to stoichiometry than their samples (polycrystalline Ti$_{1.01}$Te$_2$) and accounted for the observed residual resistivity at 5 K and Boer’s et al. [101] data did not. It is important to note, the Seebeck data in this paper. Below 150 K the S < 0 and above that S > 0 indicating a dominate carriers change. The authors’ note the thermoelectric characteristics are difficult to examine as a result of the complicated Fermi surface. It is important to note, below 10 K the Seebeck shows a minimum which suggests Ti$_{1.01}$Te$_2$ might perform optimum at this low temperature range. Boer et al. [101] argues the minimum in the hall coefficient ($\vec{H}$$\parallel$ c) and magnetic susceptibility measurements suggest CDW transitions and compares the CDW behavior in TiTe$_2$ to that of a known CDW conductor (TiSe$_2$) in the same family of materials.

Angular-resolved photoelectron spectra (ARPES) and angular resolved inverse photoelectron spectra (ARIPES) were measured by Drube et al. [102] and compared to Boer et al. [101] results. The experimental setup was performed in ultra-high vacuum for both ARPES and ARIPES experiments. Titanium Telluride (TiTe$_2$) was grown by iodine-vapor transport. It is important to note, this material, by Drube et al. [102], had an excess of tellurium in their reported stoichiometric single crystals of TiTe$_2$. The measurements were performed on samples that were cleaved from the bulk source. Drube et al. [102] ex-
periments report TiTe$_2$ band structure over a wide energy range. Good agreement is found in the with Boer et al. [101] results for the chalcogen-derived (Te) valence states observed the APRES. However, the unoccupied valence of Ti 3d band states were measured through ARIPES experiments and the results differ from Boer’s et al. [101] and Murray et al. [115] by 1.5 eV. Drube et al. [102] argues their results follow Ti 3d bands states reported by Bullet et al. (1978) that used ab initio LCAO theory. In addition to the comparison of previously reported results on the band structure of this material, Drube et al. [102] determines the work function and effective mass of TiTe$_2$. They report this material to have a work function of 5.2 eV with the ARPES experiments and an effective mass of 1.5 determined by image potential surface states in the ARIPES.

Following the reports of Boer et al. [101] and Drube et al. [102], Allen et al. [103] presents theoretical results that analyzed the theoretical and experimental results of Boer et al. [101] and Drube et al. [102]. Allen et al. [103] argues that even though Boer et al. [101] and Drube et al. [102] both confirm experimental data with band theory calculations, they did not explain the mechanism of the dispersionless band found below the Fermi level. He argues TiTe$_2$ material system is complicated since the dispersionless band is not present in theoretical models of the band structure. He shows in this paper their local density approximation (LDA) for TiTe$_2$ does not quantitatively agree with Boer’s et al. [101] APW band results. The second important finding Allen et al. [103] makes is the comparison to their calculated prediction using photoemission $\rho(T)$ data from Claessen et al. [124] to that of Boer et al. [101] and Drube et al. [102]. Allen et al. [103] points out the $\rho(T)$ of Boer et al. [101] is larger than that of Koike et al. citeKOIKE by 20% due most
likely due to the purity between the samples. Allen et al. [103] quantitatively compares the material quality through a Bloch-Grüneisen function to TiTe$_2$. Where Bloch-Grüneisen term considers electron-phonon and elastic-impurity scattering which holds true for most metals. The authors finds Koike et al. [112] results to match reasonably well as the result of pure sample. Whereas, Boer et al. [101] data deviates from between 150 K and 300 K. He suggests a possible mechanism of the differences could be Boer’s et al. [101] suggestion of CDW behavior. Allen et al. [103] further believes even greater controversy in this material regarding photoemission data and actual experimental transport data reported.

Allen et al. [103] showed the predicted $\rho (T)$ from APRES data of [124] which assumes particle-particle interaction is the only scattering extracted. The comparison of the reported experimental results of Boer et al. [101] and Koike et al. [112] leads to disagreements between APRES results and transport measurements. When Allen et al. [103] compares the APRES resistivity predictions of plane parallel to the c-axis (in-plane) to that of Boer et al. [101] and Koike et al. [112]. Allen et al. [103] finds their APRES predictions of resistivity results to be 5 times larger than experimentally reported data. They additionally show the predicted resistivity for the plane perpendicular to the c-axis (out-of-plane) to have a larger resistivity of 1700 $\mu \Omega$-cm. The authors believes APRES could be detecting surface states while transport measurements are a direct results of bulk states. It is important to note Allen et al. [103] acknowledges the possible existence of CDW behavior even though they report this material to be an ordinary metal. These result of TiTe$_2$ having ordinary metallic transport has been observed by Claessen et al. [119] with ARPES and LDA band theory calculations from a TiTe$_2$ samples grown by iodine vapor transport method and then

44
cleaved. The authors did not report characterization of $\rho(T)$ or Laue-xray diffraction to verify their stoichiometry of the sample they reported to have measured. Since TiTe$_2$ is considered a reference material for Fermi liquid system, Claessen et al. [119] addressed the discrepancies in the Ti 3d derived conduction band and suggest possible a mechanism of the dispersionless band found below the Fermi level from Boer et al. [101] and Drube et al. [102].

They theoretically observe TiTe$_2$ as a semi-metal through LDA analysis with ab initio density functional calculations using LDA band theory and linear muffin-tin orbital method in the atomic spheres approximation [119]. They agree the Te 5p valance band overlaps with the Ti 3d conduction band by 0.8 eV. However, Claessen et al. [119] studies match with Drude et al. [102] conclusions, stating the APW band theory of Ti 3d valence band calculation are in disagreement with ARIPES reported by Drube et al. [102] and LDA reported by Claessen et al. [119]. He further points out their DOS values were larger than the reported values of Boer et al. [101] and Allen et al. [103] of 1.94, 1.26, and 1.34 states per eV. Their analysis concludes that theory and experimental results agree and they did not experimentally observe a dispersionless band below the Fermi level through their high-resolution ARPES experiments. Claessen et al. [119] argues this feature is an artifact of failure in experiment set [101] by using a low-energy resolution to probe near the Fermi level and high emission angle of the ARPES experimental setup. It is important to note Claessen et al. [119] measures ARPES below 20 K and does not present compelling data to address the observed transport behaviors in Boer’s et al. [101] work.

Claessen’s et al. [119] high-resolution ARPES data was compared by Peretti et
al. [120] from the frame work of a Fermi liquid system. Peretti et al. investigated quasiparticle scattering through ARPES experiments while finding comparable agreements in their four-point probe transport measurements with temperature. Irradiation studies were also compared with measurable irradiation doses to investigate pure crystalline samples with that of disordered samples. The TiTe$_2$ samples were grown by iodine vapor transport where the samples were cleaved before measurements. From the measurements of the quasiparticle binding energy obtained from the ARPES experiments, they extracted Fermi velocity and the $\beta$ coefficient of the asymptotic expansion of the self-energy. Peretti et al. [120] found the Fermi velocity of $0.73 \pm 0.1 \text{ eV}^{-1}\text{Å}$ consistent with the LDA theory in [119]. However, Peretti et al. [120] argued, the fitting parameter $\beta = 0.7 \pm 0.2 \text{ eV}^{-1}$ is two orders of magnitude lower ($\beta = 40 \text{ eV}^{-1}$) than reported by Claessen et al. [119]. He reported Claessen et al. [119] comparison of resistivity data based on Fermi liquid electron self-energy was inaccurate [120, 103]. Additionally, he believed Claessen et al. [119] assumption of electron-electron scattering terms as the dominant mechanism of scattering was incorrect and should not have neglected other scattering mechanisms. The importance of electron-phonon scattering was later confirmed by [118].

From the frame work of the spectral properties of temperature dependent quasiparticle’s and resistivity measurements, Peretti et al. [120] found agreement between these experiments. Peretti et al. [120] showed theoretical observation of electron-phonon scattering across a wide temperature range of 4 to 300 K. This prediction closely matched the spectral line-widths from the ARPES and resistivity data across this wide temperature range which demonstrated the strong correlation between quasi-particle scattering and measured
Table 4.3: Reported Transport Behavior of TiTe$_2$ Charge Density Wave Fluctuations

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Ref</th>
<th>Reports</th>
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<tbody>
<tr>
<td>1972</td>
<td>Murray et al.</td>
<td>[115]</td>
<td>Band structure calculation</td>
</tr>
<tr>
<td>1983</td>
<td>Koike et al.</td>
<td>[112]</td>
<td>States TiTe$_2$ does not have any CDW phase transitions</td>
</tr>
<tr>
<td>1984</td>
<td>Boer et al.</td>
<td>[101]</td>
<td>Suggests CDW behavior $T = 150$ K</td>
</tr>
<tr>
<td>1987</td>
<td>Drube et al.</td>
<td>[102]</td>
<td>Confirms Boer’s and Anderson results</td>
</tr>
<tr>
<td>1994</td>
<td>Allen et al.</td>
<td>[103]</td>
<td>Suggests Boer results could be correct</td>
</tr>
<tr>
<td>1996</td>
<td>Claessen et al.</td>
<td>[119]</td>
<td>CDW transition are a result of impure material</td>
</tr>
<tr>
<td>2001</td>
<td>Perfetti et al.</td>
<td>[120]</td>
<td>States no transition found in bulk samples</td>
</tr>
<tr>
<td>2011</td>
<td>Khan et al.</td>
<td>[122]</td>
<td>CDW behavior found in thin films with light dependance.</td>
</tr>
</tbody>
</table>

transport properties. It is important to note, Peretti et al. [120] slope of the resistivity across this temperature range, closely matches Koike et al. [120] resistivity measurements. Further studies were performed by comparison a pure sample of TiTe$_2$ to that of a disordered sample from irradiation damage. Their observations lead to samples with irradiation that had the same slope as a non-irradiated sample with a higher resistivity. Peretti et al. [120] concluded TiTe$_2$ is a material with metallic transport and did not demonstrate CDW behavior.

Figure 4.2: Timeline of TiTe$_2$ investigations which show reports for both charge density wave behaviors and thermoelectric applications. Note, the author mentioned above all had the contribution of other authors (i.e., et al.). For the purposes of clarity, this section was emitted and noted here in the caption.
Based on the extensive experimental efforts of Boer et al. [101], Drube et al. [102], Allen et al. [103], Claessen et al. [119] and Peretti et al. [120], it is clear a deeper understanding of TiTe$_2$ electrical properties are needed. The summarized results are listed in table 4.3. Their reports do not clearly state the experimentally derived setup used measure resistivity nor do they report extensive studies of the material characteristics. Further investigation are needed have a deeper understanding into this controversial CDW behavior. This dissertation aims to demonstrate compelling observations of CDW behavior in through $I$ - $V$ measurements in thin films of TiTe$_2$ with a well defined material analysis. It important to note, we compared the measured resistivity of a thin sample (100 nm thick) and found data matching the predicted ARPES in-plane resistivity reports from Allen et al. [103](See table 4.2).

4.3 Titanium Telluride Exfoliation

The development of quasi-two dimensional materials has quickly progressed in the last decade with mechanical exfoliation. Mechanically exfoliated graphene revealed many interesting properties such as extremely high electron mobility [86, 125, 126] and superior thermal conductivity [94, 127], which may lead to practical applications [128, 129]. Since 2004, graphene-inspired exfoliation has paved the way to investigate new quasi-2D materials in their single layer form [74, 130]. Recently, we extended the graphene-like approach and mechanically exfoliated quasi-2D films of compound semiconductors [100, 91] to the thermoelectric and topological material domain. It was shown that quasi-2D crystals can be produced from bismuth telluride (Bi$_2$Te$_3$), which has a layered crystal structure with five
atomic planes quintuple separated by van der Waals gaps. Teweldebrhan et al. [74, 100] discovered Bi$_2$Te$_3$ quintuples are substantially different from those of the bulk crystals.

In this dissertation I show a three-layer system, titanium ditelluride (TiTe$_2$) can also be subjected to graphene-like exfoliation resulting in atomically thin crystalline films. The presence of a van der Waals gap allows one to disassemble TiTe$_2$ into its building blocks of the Te - Ti - Te tri-layers. Chiritescu et al. [92] demonstrated a TiTe$_2$ trilayer to be < 0.325 nm. The main motivation for the study of the current-voltage characteristics of the TiTe$_2$ thin crystalline films was to obtain the signatures of charge density wave (CDW) effects as we thinned from its bulk source. Previous studies in TiTe$_2$ have shown controversial debates over the presence of CDW signatures in this material in bulk [113, 112, 101, 102, 119, 120]. Boer et al. [101] found CDW signatures in TiTe$_2$ bulk form around 150 K [101]. While Claessen et al. [119] believes TiTe$_2$ has ordinary transport and that Boer et al. [101] material has stoichiometric deviations that do not preserve the 1 to 2 ratio of Ti to Te [119].

4.3.1 Crystal Properties of Exfoliated Titanium Telluride

TiTe$_2$ is a member of a distinct class of transition-metal dichalcogenide (TMD) compounds that crystallize in a space group with the characteristic cadmium-iodide (CdI$_2$)-like layer structure. It displays 6:3 coordination in which the transition-metal ion is octahedrally coordinated by the tellurium atom, with the usual stacking of A: B: A (See figure 4.3). Titanium ditelluride is a semimetal with a hexagonal crystal [131]. The lattice parameters of the hexagonal cells of TiTe$_2$ are $a = 0.377$ nm and $c = 0.6498$ nm [132]. The structure is characterized by a strong interlayer covalent bonding with the Ti - Te and weaker intralayer,
van der Waals bonding, between the Te - Te that are the adjacent tri-layers [133]. The Te - Ti - Te tri-layer film is calculated to be 0.271 nm in height from a Spartan simulation. The Te - Te spacing is found at 0.379 nm.

Figure 4.3: Schematic of 1T- TiTe2 crystal structure of space group showing tri-layers, Te - Ti - Te, and location of the van der Waals gaps. The Te - Te bond is the weakest while the Ti - Te bond is the strongest. The mechanical exfoliation results in breaking the Te - Te bonds forming the tri-layer

4.3.2 Characterization of Mechanically Exfoliated TiTe2

In order to develop technology for mechanical exfoliation of the tri-layer Te - Ti - Te, I developed a process methodology that enabled the physical material characterization TiTe2 and other layered systems (See figure 4.5). There are two main phases of material characterization before we are able to fabricate devices and analyze current-voltage properties. Phase I consists of exfoliating a layered material, transferring this exfoliated material
to a substrate and reviewing the results in an optical microscope. In the case of graphene, this process as been refined to about 5 minutes. However, newer material systems are much more challenging and require extended Phase-I development e.g. sub-20 nm Bi$_2$Te$_3$ film require about 8 hours of optical inspection when placed atop of Si/SiO$_2$. Once materials of interest have been obtained and optically identified, Phase-II of material characterization begins with Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), energy dispersive x-ray spectroscopy (EDAX), and transmission electron spectroscopy (TEM). During this phase of development, typically, Raman spectroscopy, SEM and AFM will complement each set of data from every material sample. Raman spectroscopy is a potential nanometrology tool for identifying the atomic thickness through a calibration of AFM. Moreover, Raman measurements allows one to study the phonon confinement effects as the materials geometry and volume are varied. TiTe$_2$ films were prepared by the micro-mechanical cleavage of bulk titantium ditelluride samples and transferred to a 300 nm oxide on Si/SiO$_2$ substrate (See figure 4.4). Micro-Raman spectroscopy (InVia, Renishaw) was performed in a backscattering configuration using laser excitation in the visible light ($\lambda = 488$ nm). The spectras’ were collected with a 100x objective lens using an 1800 line/mm grating to achieve a spectral resolution of 0.001 cm$^{-1}$. As a result of local heating and melting, all spectra were performed at very low power levels $P < 0.5$ mW and measured with an Orion power meter at the sample surface. At 10 percent laser power from a maximum laser power of 3.5 mW, we were able perform Raman spectroscopy measurements atop of the ultra-thin TiTe$_2$ film surface. Where ultra-thin layer are defines as $< 300$ nm. Moreover, all Raman power measurements were performed in
Figure 4.4: (a) - (d) Images of the quasi-2D crystals showing SEM images of the exfoliated quasi 2D crystal flakes ≤ 100nm in height. These SEM images clearly demonstrate TiTe$_2$ is able to be mechanically exfoliated and transferred to Si/SiO$_2$. (e) Provides the AFM micrographs of the flakes found in (c). It is important to note, sub 100 nm flake are not visible optically

one location with wavenumbers that relative to the laser excitation of 488 nm. We report details of our Raman instrumentation procedures earlier in the context of graphene investigation [134, 135, 136]. The vibrations for the Raman modes are shown in (b) of Figure 4.3
Figure 4.5: Material characterization process developed to identify mechanically exfoliated films, material identification, atomic percents, absolute height scales, and crystallinity of any layered material system

and (c) of Figure 4.3. These Raman modes are characteristic of CdI$_2$-like-structures with space group space symmetry. These CdI$_2$-like structures have 6 normal optical modes for lattice vibrations [137].

Unlike Bi$_2$Te$_3$, titanium ditelluride has two Raman active modes produced entirely by the chalcogenide atom (Te) for both the in-plane, $E_g$-peak, and out of plane, $A_g$-peak with the transition-metal atom (Ti) at rest [138]. Using a laser power with a wavelength of 488 nm, I have observed $E_g$ and $A_g$ peaks at 120 and 140 cm$^{-1}$, respectively (see Figure 4.6) using relative wavenumbers. It is clear the Raman spectrum is produced entirely by the chalcogenide atom (Te). From observations with the EDAX spectrum the tellurium
Figure 4.6: Raman spectrum of graphene-like mechanically exfoliated flakes of atomically thin quasi-2D crystals of titanium ditelluride (TiTe$_2$). (a) - (b) shows the Raman spectrums as a function of varying laser power. In (c) the E$_g$ peak, in-plane vibration, dependence verses power for 300nm and 100nm film heights; (d) Shows the A$_g$ peak, out-of-plane dependence verses power for 300nm and 100nm film heights. It is important to note that the known Raman intensities are sensitive to volume changes in materials.

atom is predominate and break the 1 to 2 titanium to tellurium atom. As I increased the power in the sample, I began to observe two distinct features: (1) E$_g$ peak started showing a red shift with increasing power; (2) A$_{1g}$ peak intensities began to increase at certain powers and then fall again as we approached 100% power. After each measurement, we
verified material quality via the optical microscope on the Raman instrument. Optically, the material appears discolored after the laser power excitation is above 30% to 50% (See (a) and (b) in figure 4.6). These Raman features are suggestive of melting, however, the Raman spectrum still produces the same fingerprint. It is possible impurities, breaking of bonds, dislocation, or disorder could be induced once the film cools and recrystallizes from local heating of the laser spot. It is important to note, the shoulder found in the A$_{1g}$ peak at 90% power may indicate possible forms of impurities [139]. Raman irradiation of CDW material could show pronounced CDW effect in the current-voltage measurements. Further studies are needed here to laser irradiation CDW materials. These laser power dependence studies suggested very low values of the thermal conductivity.

The strong spatial confinement of charge carriers and phonons allow one to tune the quasi-2D crystals properties and obtain unique functionality for different applications. Strong spatial confinements of phonons are clearly observed in mechanically exfoliated TiTe$_2$. We clearly observed a reduction in peak intensities when we compared the in-plane (E$_g$) peak with varying heights scales (See (c) - (d) in figure 4.6). Since the in-plane vibrations are not substrate dependent we are able to conclude these data are characteristic of flake heights. Due to the fact the out-of-plane vibrations are substrate dependent, the A$_{1g}$ peak should produce different characteristics at increasing power with other substrates (e.g. mica, sapphire, oxides, or metals). The Raman data we report are characteristic of Si/SiO$_2$ substrates. Additionally, I would like to note a peak at 261 cm$^{-1}$ occurs. This peak is found in our Raman spectrum and documented as an IR active peak (12). Further IR studies are needed to verify this peak behavior. Moreover, these data suggests that Raman
spectroscopy can be used as a nanometerology tool for characterization of the atomically thin films of TiTe$_2$. Both films were studied with the AFM to verify the step height. The isolated TiTe$_2$ flakes were examined using a high-resolution scanning electron microscope (XL-30 FEG) operated at 10-15 kV (See figure 4.4).

The lateral height dimensions studies were performed using a VEECO AFM Dimension 5000 with vertical resolution down to 0.1 nm. I did optically detect flakes through a purplish tint in two samples. Such optical contrasting has been observed in other quasi-2D materials atop 300 nm Si/SiO$_2$ wafers [97, 140]. However, in this study, purplish tint of TiTe$_2$ shows a material height of 170 nm. EDAX studies have been perform to verify the elementary composition and stoichiometry of the exfoliated thin film. Preliminary data suggest that the bulk TiTe$_2$ crystals have a 2% deviation in tellurium (TiTe$_{1.96}$). Rigorous stoichiometric analysis is needed to quantitatively justify the exact atomic percent.

4.4 Electrical Characterization of Titanium Telluride Crystals

4.4.1 Charge Density Wave Theory

The CDW conductors are usually characterized by non-linear current-voltage (I-V) curves and electrical anisotropy. The CDW is a low-dimensional transport phenomenon involving strong electron phonon coupling [141]. This strong interaction breaks the translational symmetry of the crystal through a phase change and creates current known as collective CDW current [142]. Where the CDW current is the collective motion of the charged carriers. This
phenomenon referred to as charge density waves (CDW) was rst discovered in transition-metal dichalcogenides TMDs from the metallic group Vb [111, 143, 144, 145]. Within specific temperature ranges, $T_{p1}$ and $T_{p2}$, CDW transitions are induced and electrons begin to exhibit a new periodicity with newly formed lattice deformation [142] [146]. The lattice phase change occurs as a result of a Peierls transitions. Where the Peierls transition temperature identifies the temperature threshold of a CDW conductor where a phase change occurs. These phase changes are identified as incommensurate (IC) phase, commensurate (C) phase, and quasiconmensurate (QC) phase [147]. Table 4.4 provide examples of phase transitions in known bulk CDW conductors. Each phase will identify at which temperature ranges these phases occur indicating a lattice deformation. The charged carriers are periodically modulated in space by a CDW amplitude, phase and Fermi wavevector [148].

In literature to-date, CDW electrical properties have been studied based on a four probe configuration [151]. This four probe configuration used two approaches noted normal and transposed with a CDW conductor as the channel (See figure 4.7). Here the normal configuration is where a current is applied from the outer probes and the voltage measured form the inner probes. In the transposed configuration the current is applied from the inner probes and the voltage read from the outer probes. The $I - V$ characteristics produce a non-linear relationship. In both cases, a certain voltage range will produce no current.

<table>
<thead>
<tr>
<th>CDW Conductors</th>
<th>1T-TaS$_2$ [147]</th>
<th>NbSe$_3$ [149]</th>
<th>2H-NbSe$_2$ [150]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$ (K)</td>
<td>350</td>
<td>144</td>
<td>35</td>
</tr>
<tr>
<td>$T_2$ (K)</td>
<td>180</td>
<td>54</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.4: CDW Phase Transitions from Metallic Group Vb
Figure 4.7: Demonstrates $I - V$ experimental setup in a four-probe configuration as shown by Gill et al. [151] (a) shows the normal configuration where current is applied in the outer probes and voltage is measured in the inner probes (b) shows the transposed configuration where current is applied in the inner probes and the voltage is measured in the outer probes.

After a certain voltage is applied (voltage threshold ($V_T$)), current is measured across the measured channel. When the channel turns on, the CDW current is noted to be depinned from impurities and allowed to flow. In the normal configuration the $V_T < V_T$ of the transposed configuration. Since the electric field penetration is shallow, a larger amount of current is needed for depinning in the transposed configuration. The CDW current is said to be depinned when the applied voltage is $> V_T$. Furthermore, if one compares the $I - V$ curves from the normal and transposed configurations at a specific current one would observe there is a clear difference in voltage. Gill [152] suggested the additional voltage ($V_{normal}(I_c) - V_{transposed}(I_c)$) in the transposed configuration as a phase-slip voltage ($V_{ps}$). This behavior is attributed to compression at one contact while stretching at another contact due to the movement of the CDW current.
4.4.2 Device Fabrication Processes and Methodology

A cleanroom based device fabrication was implemented to pattern two contacts atop of the sample under test (SUT). The fabrication steps consisted of transferring the sample on top of a Si/SiO\textsubscript{2} substrate via scotch tape. Here the Si substrate is highly doped so that the conductive semiconductor behaves like a metal contact. The SiO\textsubscript{2} layer has a thickness of 300 nm and will be used as the oxide for the back-gating the SUT. During device fabrication process (See figure 4.8), the substrate is spin coated on a Headway/SCE tool where two copolymer (MMA) and polymethyl methacrylate (PMMA) positive resist are deposited at specified dwell time/rates and spin time/rates. The spin times and rates are based the required thickness which need to be three times the thickness of the SUT. The substrate is hard baked after each spin coat. Next a pattern can be form with either a photolithography mask aligner or electron beam lithography (EBL) system. This process utilized a Leo 1150 EBL fabrication tool to exposed a custom pattern in the MMA and PMMA photoresist layers. The substrate is then placed in a developer to etch the pattern and expose the surface for metallization to be deposited. Before metal deposition, the substrate should be dipped in buffered oxide etch (BOE) to remove any organics at the surface (i.e. contamination from the polymer) of the sample and substrate. An electron beam evaporator was used to deposit two metal layers atop of the PMMA and exposed areas. Lift off is performed by setting the substrate in acetone for some amount of time to etch away the photoresist layers leaving only the SUT with contacts attached. For titanium telluride, lift off would also remove the sample from the substrate and the process was started over to increase the device fabrication yield.
4.4.3 Electrical Characterization and Analysis

We were able to fabricate the back-gated field-effect transistor (FET) type devices with TiTe$_2$ as the conduction channels. Figure 4.9 shows the measured source-drain current ($I_{ds}$) as a function of the source-drain voltage ($V_{ds}$) at different gate biases and gate voltages. One can see that our $I_d - V_d$ is highly non-linear for a metallic channel. This current strongly increases when the voltage reaches a certain threshold voltage $V_T$. This behavior is similar to the one observed in known CDW materials. The on-and-off state switching is not as pronounced as in some other CDW materials possibly because the transition temperature in TiTe$_2$ in bulk form is below RT [101]. Conduction by the TiTe$_2$ channel was measured as a function of back-gate voltage ($V_g$) at RT (See figure 2b). The large gate voltage is due to the 300 nm thick oxide. As we swept the gate voltage from negative
to positive, we observed multiple sharp peaks at specific gate voltages. To justify the experimentally observed changes in carrier concentration across the channel, in the $I_d-V_g$ curve at specific gate voltages, we theoretically analyzed the change in Fermi wavevector and Debye screening length between the 8 $\mu$ contact spacing for a single tri-layer \cite{153}. From D. K. G. de Boer et al. \cite{101} estimate of the electron density of 0.052 electron and 

Figure 4.9: Electrical characteristics of FET type devices with the channel made from the 100 nm crystalline thin film of TiTe$_2$ at RT. a) the presence of the voltage threshold for the on-set of the electrical current suggests the CDW behavior as the gate voltage is varied. The inset shows how temperature induced sliding wave. b) Id-Vg curves showing the gate voltage produces a large modulation in the TiTe$_2$ channel.
holes per unit cell, we were able to estimate the unit cell volume. The unit cell volume is \( V_c = a \cdot b \times c = a^2ccos(60^\circ) = 46.35 \text{Å}^3 \) Where the the electron and hole density per volume and sheet density per layer defined respectively as:

\[
n = \frac{0.052}{46.35 \text{ Å}^3} \left( \frac{10^8 \text{ Å}}{\text{cm}} \right)^3 = 1.12 \times 10^{13} / \text{cm}^3 \tag{4.1}
\]

\[
n_L = 1.12 \times 10^{21} c = (1.12 \times 10^{21}) (6.5 \text{ Å}) \left( \frac{1 \text{ cm}}{10^8 \text{ Å}} \right) = 7.28 \times 10^{13} \text{ cm}^2 \tag{4.2}
\]

The Fermi surface is complex with multiple disconnected parts in the \( k_x - k_y \) plane with small dependence in the \( k_z \) plane. Theoretical analysis is performed by approximating the Brillouin zone and Fermi surface as square in the \( k_x - k_y \) plane.

\[
n_L = 2 \int_{-k_{fx}}^{k_{fx}} \frac{dk_x}{2\pi} \int_{-k_{fy}}^{k_{fy}} \frac{dk_y}{2\pi}
\]

\[
n_L = \frac{2}{\pi^2} = 7.28 \times 10^{13} / \text{cm}^2 \tag{4.3}
\]

where \( k_{fx} = k_{fy} \). We defined a normalized Fermi wavevector as \( k_f = \tilde{k}_f \left( \frac{\pi}{a} \right) \). Where \( \tilde{k}_f \) is the normalized wavevector. From equation 4.3 the un-perturbed sheet density is defined as:

\[
n_L = \frac{2}{\pi^2} \left( \frac{\pi}{a} \tilde{k}_f \right)^2 = \left( \frac{2}{a^2} \right) \tilde{k}_f^2 \tag{4.4}
\]

Solving for the normalized Fermi wavevector \( \tilde{k}_f \) to analytically understand the how Fermi wavevector for this material system change under an an applied voltage, we find \( \tilde{k}_f \) results in:

\[
\tilde{k}_f = \sqrt{\frac{n_L a^2}{2}} = \sqrt{\frac{(7.28 \times 10^{13})(3.78 \times 10^{-8})^2}{2}} = 0.23 \tag{4.5}
\]
\[ k_f = 0.23 \frac{\pi}{a} \]  \hspace{1cm} (4.6)

To interpret how the Fermi wavevector is changing at these spikes with an applied gate voltage, at a specific contact spacing (L), we analyze the change in the Fermi wavevector, \( \delta k_L \), and the Debye screening length \( \lambda_D \). We believe the spikes observed in the \( I_d - V_d \) curves are a result of new CDW being added or removed. If we analyze whether \( \delta k L = 1 \), we will be able to justify the CDW phase has changed by \( 2\pi \). It is important to note this factor shows us if a new wave is being added or subtracted during these spikes being observed. In this 100 nm thick sample at a gate voltage of 20 volts and an oxide thickness of 300 nm, we assume the charge is evenly distributed across the thickness of the film. The change in charge with applied gate voltage is:

\[
\delta n_c = \frac{CV}{q} = \left( \frac{8.854 \times 10^{-14} \times 3.9 \times 20}{300 \times 10^{-7} \times 1.602 \times 10^{-19}} \right) \hspace{1cm} (4.7)
\]

Here it is important to note, the 20 V corresponds to the voltage spike feature in the \( I_d - V_G \) curve. Since a 100 nm thick film has 153.9 tri-layers the approximately induced charge, \( \delta n_c \) in equation 4.7. If this charge is were evenly distributed across the thickness of the film, the induced charge per tri-layer would be:

\[
n_{Lo} = \frac{2}{\pi^2} k_f^2 \hspace{1cm} (4.8)
\]

When the material is under gate bias, the sheet density and change is charge with gate voltage is defined respectively as:

\[
n_{Lo} = \frac{2}{\pi^2} (k_f + \delta k)^2 \hspace{1cm} (4.9)
\]

\(^1\)Theoretical analysis is after R. K. Lake (unpublished)
\[
\delta n_{Lo} = \frac{2}{\pi^2} 2k_f \delta k = \frac{4k_f \delta k}{\pi^2}
\]  

(4.10)

Here we have ignore the \((\delta k)\) term based on the dat obtained below. The change in the Fermi wavevector, \(\delta k_f\), and the \(\delta k_f L\) is:

\[
\delta k_f = \frac{\delta n_L \pi^2}{4k_f \alpha} = \frac{(9.357 \times 10^9)(\pi^2)(3.78 \times 10^{-8})}{4(0.23)\pi}
\]

(4.11)

\[
\delta k = 1207cm^{-1}
\]

(4.12)

\[
\delta k L = 1207(8 \times 10^{-4}) = 0.965
\]

(4.13)

Since \(\delta k\) is approximately 1, we can quantitatively observe the possibility of a CDW having a \(2 \pi\) phase change at the 8 \(\mu\) contact spacing and a 20 V applied gate voltage. Since our \(I_d - V_G\) curve do not show the full maximum it is reasonable see a slightly higher gate voltage would produce a full \(2 \pi\) phase change. The Debye screening length is defined as follows \(^2\):

\[
\lambda = \sqrt{\frac{\epsilon k_B T}{n q^2}} = \sqrt{\frac{8.854 \times 10^{-14}(F/m)0.026(V)}{1.12 \times 10^{21}(cm^3)1.602 \times 10^{-19}(C)}}
\]

(4.14)

\[
\lambda = 3.58 \times 10^{-9} \text{ cm} = 0.036 \text{ nm}
\]

Where \(\epsilon\) is the relative dielectric constant assumed to be 1, \(k_B\) is the Boltzman’s constant, \(T\) is the absolute temperature, \(n\) is the the electron (and hole) density \([101]\), and \(q\) is the electron charge. Since the screening length is sub nanometer the potential beyond the first trilayer should be unaffected by the gate voltage. Furthermore, the previous assumption regarding the induced charge being uniform across the film is hard to justify. More work needs to be done to reconcile the short screening length with our experimentally observed \(I_d-V_g\) data as well as validating the uniformity of the induced charge across the film under gate bias.

\(^2\)Theoretical analysis is after by R. K. Lake (unpublished)
4.4.4 Summary of Electrical Characterization

Using graphene-like mechanical exfoliation, we obtained single crystals of atomically thin films of TiTe$_2$, and fabricated the back-gated field-effect devices. The back-gated current-voltage characteristics of the TiTe$_2$ devices revealed strong non-linearity in a metal, which is attributed to the charge-density wave effects. The TiTe$_2$ crystal demonstrate a clear dependence on light during the $I-V$ experiments. When light is present, the $I-V$ signature were clearly different. When the device was exposed to light, the $I-V$ have a monatomic dependance that is characteristic of metals. When the optical microscope light was turned off and the device was only exposed to indirect light (e.g. semi-dark) the $I-V$ signature was highly non-linear. This non-linearity characteristic of CDW behavior. The TiTe$_2$ quasi-2D material demonstrates a clear $I_{G}$-$V_{G}$ gating effect that has not been reported in literature to-date. The quasi-2D crystal demonstrate the possibility of a metal-to-semiconductor transition under the CDW behavior at RT. The back-gating function in our TiTe$_2$ devices was not as good as in graphene FETs but better than in devices fabricated with exfoliated Bi$_2$Te$_3$ films. The obtained results are important for the proposed application of TiTe$_2$ for the charge-density wave materials and thermoelectric energy conversion.
Chapter 5

Nanostructured Materials for
Electrochemical Energy Storage

5.1 Nanostructured Electrodes in Electrochemical Storage Cells

5.1.1 Motivation of Electrode Design for Energy Storage and Generation

The maximum energy converted by the electrochemical reaction is not equivalent to energy being transferred to the load as a result of losses in the material and electrochemical reactions at the interface of the electrode. The loss of free energy at the electrode surface is a direct result of chemical reactions [154], surface passivation [155], electrical resistance [156, 157, 158], and intrinsic thermal properties of the electrodes [46, 159, 160]. It is important to note, the discharged current of a cell is proportional to the electrode area [40].
Figure 5.1: Commercial trend in Li-ion research and development which demonstrates the emerging markets for highly efficient Li-ion batteries for portable electronics or high power density Li-ion batteries for power tools and medical devices [43].

The thermal and electrical degradation have been shown to affect primary, secondary and reserve batteries including materials composed of lithium-ion [46, 161, 154], nickel-metal [160], sodium-sulfide [162], sodium-nickel chloride (ZEBRA) [163] and lead-acid [49].

The Li-ion batteries have been the electrochemistry of choice for the long cell life and electrochemical stability [13, 43]. Li-ion technologies have a billion dollar market for applications, research and development to improve the efficiencies in the electrochemical cells for portable electronics, while in parallel looking for lower cost materials for high power density applications needed in an emerging electric vehicles market (See figure 5.1) [13, 43, 9, 164]. In the former case, Li-ion batteries are limited to larger specific capacities and have reached a limit with LiCoO$_2$/graphite electrodes [43]. The latter case, has created a demand for electrodes with higher specific capacities that can deliver higher currents at faster rates for power density applications. Electrode material and geometry has been
under much investigation to find methods in delivering faster discharging/charging rates at higher energy densities [165, 166]. However, the faster discharging/charging requires high current densities which create large polarization effects. Maleki et al. [161] demonstrates the thermal behaviors of Li-ion batteries with respect to the electrodes thermal properties in commercially available Sony batteries are dependent on the electrode material. Saito et al. [156] shows mechanisms of thermal transport (ohmic polarization) in Li-ion batteries is a result charging and discharging in the electrode.

5.1.2 Significance of Designing Nanostructured Electrodes

Nanostructured electrodes present an novel development to address the concerns of finding a higher specific capacities concerning energy and power densities with improved charge/discharge efficiencies in electrodes of an electrochemical cell [14]. Nishizawa et al. [14] experimentally compared LiMn$_2$O$_4$ hollow nanotubes to a film electrode and discovered a 2.5 to 12 times greater specific capacity at increasing current densities in the nanotubes as compared to a film composed of grains sizes of 500 nm, respectively. Since it was known the smaller grain sizes produced higher specific capacities, the author fabricated 50 nm nanotubes. Nishizawa et al. [14] argues 90% of the nanotube was used versus 35% of the film as a result of increased surface area and lower Li$^+$ diffusion lengths. They observe the increased surface area allowed more intercalation sites and lowered Li$^+$ ion diffusion lengths to increase the rate of discharging and charging capacity at increased current densities (See figure 5.2). Nishizawa et al. [14] discovered significant results to support a new direction in higher specific capacities with larger current, discharging and charging densities. However, Nishizawa
et al. [14] does not address the surface passivation layers that occur in alkali earth metals such as lithium [155] which creates lower specific capacities and irreversible behavior on the LiMnO$_4$ electrode [44]. A review of more recently designed nanostructured electrodes which address solid electrolyte interphase formation can be found in [9]. Surface passivation was discovered by Peled et al. [155] and is referred to as solid electrolyte interphase (SEI). These surface passivation layers occurs when an alkali and alkaline earth metal are in contact with aqueous and non-aqueous electrolytes. Since the Li$^+$ ions are rocked from the anode to the cathode, both electrodes will form an SEI layer [167]. The SEI layer is a non-soluble film on the surface of the metal which has a layer formation rate and thickness dependence based on the surface area during passivation and the electron tunneling range [155, 168].
One should note, the mechanism for SEI formation is different in aqueous and non-aqueous electrolytes and must be maintained in certain temperature ranges. This layer is a cationic conductor and electronically insulating while maintaining reversibility through the Nernst Law [155]. A deeper understanding in SEI formation can be found in [169]. In current lithium-ion technologies, increased surface-to-volume ratios on the anode and cathode is needed for high Li\(^+\) intercalation to developed faster processes in high performing energy storage and generation batteries.

The significance of nanostructured electrodes creates smaller diffusion lengths for lithium insertion and removal [14, 170, 171]. The diffusion lengths defines the amount of time it takes for Li\(^+\) insertion or removal is proportional to the square of the diffusion length of the electrode (See equation 5.2). Assuming one dimensional transport in a solid, the diffusion coefficient obeys Fick’s second law where the electrolyte/electrode interface, local concentrations are expressed relative to the time and distance at the interface [172]. Wen et al. [172, 171, 173] expresses the diffusion lengths in terms of a diffusion time constant as: 5.1):

\[
\frac{t}{\tilde{D}} = \frac{L^2}{\tilde{D}} \quad \text{(sec)}
\]

where \( t \) is the diffusion time constant, \( L \) is the diffusion length or volume to surface ratio, and \( \tilde{D} \) is the diffusion coefficient. Wen’s definition is a quantitative description to provide information into the length of time Li\(^+\) intercalation and removal takes based on the known parameters of geometry and diffusion coefficient. Figure 5.3 illustrates nanostructure time constant at specific radiuses and diffusion coefficients. However, the diffusion coefficient is complex and varies with temperature. A more accurate description for calculating the
Figure 5.3: Log-log diffusion time constant (after Wen’s et al. [172] definition in equation 5.1 modeled for nanostructured geometries of a cylinder and sphere as a function of varying geometries. The Diffusion length is accounted for through the surface-to-volume ratio of each geometry. It is clearly shown faster discharging/charging times can be acheived with sub 50 nm radiuses at the specified diffusion lengths.

diffusion coefficient for Li$^+$ ion diffusion is given by Weppner et al. [170]. The diffusion coefficient $\tilde{D}$ can be calculated experimentally by a galvanostatic intermittent titration technique as derived by Weppner et al. [170] (See equation 5.2).

$$\tilde{D} = \frac{4}{\pi \tau} \left( \frac{m_B V_M}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \text{ where } \left( \tau << \frac{L^2}{\tilde{D}} \right)$$  \hspace{1cm} (5.2)

Here $\tau$ is a constant current pulse time, $m_B$ is the molar mass, $V_M$ is the molar volume,
$M_B$ is the molar mass of the insertion electrode material, $S$ is the area of the electrode-electrolyte interface, $\Delta E_s$ is the change in steady-state voltage during a single-step, and $\Delta E_t$ is the total change of the cell voltage during a constant current pulse $\tau$ of a single step that is neglecting ohmic polarization [170, 174]. Weppner et al. [170] assumes the intrinsic coefficient of one species is equal to the interdiffusion coefficient of two atomic species assuming there is either two ionic species or one ionic species and one electronic species dominate in the interdiffusion coefficient transport phenomenon. It is important to note the ratio $(m_B V_M)/M_B$ is the volume of the electrode. This indicates the diffusion time constant is complicated and not easily reduced based on the reduced diffusion length since the diffusion coefficient is inversely proportional to the square of the surface to volume ratio and sensitive to the operating temperature.

By nanostructuring electrodes based on Li$^+$ ion diffusion it is possible to design faster discharging/charging rates at higher currents and capacities [9, 175]. However, other resistive parameters such as the ion transport through the electrolyte, electrochemical en intrinsic electric properties and electrode thermal conductivity [175, 157, 176, 177]. Furthermore, energy storage and generation efficiencies are interdependent on the intrinsic and extrinsic thermal properties within the electrodes and electrolyte [46, 159, 161, 156, 154, 160, 162, 163]. This chapter addresses the thermal and electrical characterization carried out on nanostructured anodes in collaboration with Georgia Institute of Technology [178]. Higher power factors are dependent on discharging/charging densities that produce large current densities. The main factor leading to larger discharging/charging densities and specific capacity depends on the amount of Li$^+$ ions that can be inserted per molecule, atom or
unit cell volume [41], diffusion lengths, surface-to-volume [14], and specific capacity of the electrode [41]. See table 5.1 for a list of specific capacities for electrode materials. Important

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Specific Capacity</th>
<th>Electrode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Nanowire</td>
<td>4277 mAh/g</td>
<td>Anode</td>
<td>[12]</td>
</tr>
<tr>
<td>Silicon</td>
<td>Nanocomposite</td>
<td>3500 mAh/g</td>
<td>Anode</td>
<td>[179]</td>
</tr>
<tr>
<td>Li_{4.4}Si</td>
<td>Alloy</td>
<td>3600 mAh/g</td>
<td>Anode</td>
<td>[180, 181]</td>
</tr>
<tr>
<td>Si-C</td>
<td>Nanocomposite</td>
<td>700 mAh/g</td>
<td>Anode</td>
<td>[182]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Nanocomposite</td>
<td>600 mAh/g</td>
<td>Anode</td>
<td>[183]</td>
</tr>
<tr>
<td>Carbon</td>
<td>Nanotubuals</td>
<td>490 mAh/g</td>
<td>Anode</td>
<td>[177]</td>
</tr>
<tr>
<td>TiO₂-B</td>
<td>Nanowires</td>
<td>200 mAh/g</td>
<td>Anode</td>
<td>[184]</td>
</tr>
<tr>
<td>Graphite</td>
<td>Nanocomposites</td>
<td>372 mAh/g</td>
<td>Anode</td>
<td>[9]</td>
</tr>
<tr>
<td>Li-CoMnO</td>
<td>Nanowires</td>
<td>230 mAh/g</td>
<td>Cathode</td>
<td>[45]</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>Nanowires</td>
<td>110 mAh/g</td>
<td>Cathode</td>
<td>[44]</td>
</tr>
</tbody>
</table>

observation to achieve high specific capacities were first investigated by Sharma et al. [181] and Boukamp et al. [180]. Boukamp et al. [180] built on the work of Sharma et al. [181] by demonstrating Li⁺ insertion into silicon produced a range of Li-Si alloys based on the phase [181]. LiₓSi alloy where 0 ≥ x ≤ 4.4 produces the most stable alloy with the highest specific capacities to date. The alloy Li_{4.4}Si produces a specific capacity of 4200 mAh/g by accommodating 4 Li atoms to 1 silicon atom which is justified by demonstrating the Si unit cell volume is 3 times larger than that of bulk [41]. This increased volume will be a major concerns when silicon is nanostructured to increase the Li⁺ insertion and removal [12].

Tin based composite oxides have also been found to have high specific capacities > 600 mAh/g. In the oxide form, Tin(II) Oxide (SnO₂) accommodates Li⁺ insertion in its active center [183]. When comparing the specific capacities of the electrode, it is clear the lower specific capacities are a results of less Li⁺ ions per volume or atom.
Table 5.2: Review of State-of-the-Art Core/Shell Nanostructured Electrodes

<table>
<thead>
<tr>
<th>Core/Shell</th>
<th>Specific Capacity</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT/Si/Carbon</td>
<td>3200 mAh/g</td>
<td>Highly Ordered</td>
<td>[178]</td>
</tr>
<tr>
<td>Si/C</td>
<td>1137 mAh/g</td>
<td>Nanocomposite</td>
<td>[167]</td>
</tr>
<tr>
<td>CNT/MnO$_4$</td>
<td>1000 mAh/g</td>
<td>Highly Ordered</td>
<td>[185]</td>
</tr>
<tr>
<td>SnO$_2$/CNT</td>
<td>600 mAh/g</td>
<td>Highly Ordered, Hollow Core</td>
<td>[154]</td>
</tr>
<tr>
<td>SnO$_2$/Carbon</td>
<td>400 mAh/g</td>
<td>Highly Ordered</td>
<td>[177]</td>
</tr>
</tbody>
</table>

5.2 State-of-the-Art Nanostructured Electrodes

Advanced performance has been observed with nanowires that have an inner core and outer shell [154, 157, 176, 185]. The novelty of creating coated nanowires enables the electrode material to combine high specific capacity through larger Li$^+$ ion insertion per volume [183] in one layer, with increased electrical and thermal properties of a second layer [186]. The core/shell technology combines the strengths of material properties for higher specific capacities, higher thermal diffusivities, and lower resistivity (See table 5.2). Materials designed in proof-of-concept experiments have shown investigations of nanowires with materials including LiMn$_2$O$_4$ [44], Li$_{0.88}$Li$_{0.18}$Co$_{0.33}$Mn$_{0.44}$O$_2$ [45], core-shell silicon and silicon [157, 12], SnO$_2$ [165], Co$_3$O$_4$ [187]. More notable material synthesis has been creating 1D nanostructure’s with coatings on the outside layer to combine the electronic, thermal and physical properties into one nanowire array structure. These material architectures include SnO$_2$ coated with carbon [176], CNTs have been used as either a core or shell in core/shells of MnO$_2$ and SnO$_2$ [177, 154, 185], respectively. The motivation of SnO$_2$ nanowires is the high capacity Li-ion intercalation with good cyclic durability. Idota et al. [183] reports using SnO$_2$ as a negative electrode with a various positive electrodes to produce capacities.
that exceed nickel hydride cells. However, Huang et al. [165] demonstrates SnO$_2$ nanowires suffer from large volume expansion. Zhoa et al. [176] later investigated SnO$_2$ nanowires coated with amorphous carbon nanotube (a-CNT) to combine the high reversible capacity of Li-ions with carbons materials of high thermal [30, 31] and electrical properties [188].

Zhoa et al. [176] data demonstrates the stress found in SnO$_2$ nanowires is reduced. Wang et al. [154] reports a similar structure with hollow SnO$_2$ coated with carbon nanotubes (CNTs). This nanostructure shows the hollow SnO$_2$ with CNTs displaced the stress reported in SnO$_2$ while enhancing the electrical conductivity and Li-ion transport. Reports of CNTs properties as a negative electrode can be found reports by Che et al. [177]. CNTs were motivated by the increase of the surface-to-volume of electrode/electrolyte and reversibly with Li$^+$ as compared to the previous carbon negative electrodes. In contrast to Che et al. [177], Mohana et al. [185] creates a core/shell of CNTs coated with MnO$_2$. This enable Li$^+$ ions to diffusive mainly through the MnO$_2$ shell with the path of least resistance through the CNT core. Additionally, CNT core provide a diffusive path of heat from polarization effects. They report CNT synthesis as the inner shell with MnO$_2$ coated on the outer shell. These results demonstrate that CNTs alleviate the high volume expansion of MnO$_2$ while intercalation sites for Li-ions in both the core and shell materials. Such observations by Zhoa et al. [176], Wang et al. [154] and Che et al. [177] provide increased motivation to further investigate the true value CNTs will have in the energy storage and generation.
5.3 Experimental Setup for Thermal Conductivity and Electrical Resistivity Characterization

5.3.1 Experimental Setup for Cross-Plane Thermal Measurements

We have carried out thermal characterization of the batteries with MW-CNT electrodes which are discussed in depth in the next section [178]. The thermal conductivity was measured using a noncontact optical laser flash technique (LFT). In the LFT (NETZSCH) measurement, a xenon flash lamp produced shots with an energy of 10 J/pulse on the sample surface while the temperature rise was measured at the other end with an InSb infrared (IR) detector. The InSb IR detector is equipped with an integral dewar for liquid nitrogen cooling to keep the detector at 77 K (See Figure 5.4). The xenon flash lamp has user selectable pulse widths (i.e. 100 µs, 400 µs, and 700 µs) to allow for accurate tuning of the transient voltage response. Here one should note the importance of sample preparation. Due to basic limitations of the experimental analysis of this LFA 447 NETZSCH instrument, certain geometries and thickness are required for the sample under test. The thermal-wave travel time allows us to measure the thermal diffusivity $\alpha$. The thermal conductivity $K$ is related to $\alpha$ as $K = \alpha \rho C_p$, where $\rho$ and $C_p$ are the mass density and specific heat of the material, respectively. Details of the experimental setup and measurement procedures were reported by us elsewhere [77, 78, 79]. The system used for this study was calibrated with other techniques for measuring thermal conductivity such as transient planar source and 3-omega techniques [79] [80, 81]. The $K$ values measured for given samples are associated with the cross-plane thermal conductivity, i.e. along the MW-CNT length, as determined
Figure 5.4: Laser flash can be used to measure thermal properties of a range of materials. The experimental setup of the laser flash includes optical stage for the sample under test, optical mask, infrared detector, mixed signal circuit, temperature control and xenon lamp and controls. It is important to note, the optical stage is custom designed when material under test do not have the specified geometry.

by the experimental setup and direction of the temperature gradient (See figure 5.5).

Figure 5.5: Demonstrates the experimental setup to establish the thermal conductivity measurements across a range of temperatures. The image to the left provides and expanded view of the sample in the sample holder. The right image illustrates the top view of the optical mask and sample that is in sensing range of the IR detector.
Figure 5.6: Demonstrates the experimental setup to establish the electrical resistivities across range of temperatures ranging from 25°C to 90°C. This two probe setup varied the voltage while measuring the current at each voltage increment of 20 mV. The resistivity at each temperature was measured across a voltage range of -1 V to 1 V.

5.3.2 Experimental Setup for Cross-Plane Electrical Measurements

The electrical measurements were performed using a two-probe technique to measure $I$ - $V$ characteristics using an Agilent B1500A analyzer and a micromanipulator probing station. The probes that made contact to the electrodes were made of tungsten metal with a tip radius of 0.5 microns. Resistivity is measured by sweeping a voltage from -1 V to 1 V in 20 mV increments across a temperature range of 25 to 90 Degree C in the cross plane direction of the electrode. The experimental setup established the resistivity of the electrode, that included both the vertically aligned carbon nanotube (VACNT) material and copper substrate (See figure 5.6). Based on the parameters of the experimental setup, the resistivity measurements demonstrate the electrical properties in the cross-plane thermal conductivity, i.e. along the MW-CNT length.
5.4 Thermal and Electrical Properties of Li-ion Electrodes

5.4.1 Thermal Conductivity Temperature Dependence in CNT Arrays

The CNT electrode is placed on 12.6 mm square copper foils that are attached with a thin layer of epoxy (See figure 5.5). Slight modifications are made to the optical stage to prevent light leaking through and shining on the IR detector. The thermal conductivity measurements are performed over a temperature range of 25 °C to 90 °C for all the electrode samples. The wider range thermal conductivity measurements were limited to low thermal conductivity of the epoxy used to adhere the CNT material to the copper substrate. A double-layer model was developed to extract the thermal diffusivity and thermal conductivity of the MWCNT/Si/C material. The model accounted for the heat loss and contact resistance between the copper and carbon layers. Figure 5.7 shows the results of the measurements for the MWCNT/Si/C electrode, a reference Si powder/carbon black pellet and Si powder/carbon black electrode pellet. One can see that effective thermal conductivity $K$ determined for the CNT coated with silicon/carbon (CNT/Si/C) structure is in the range $\sim$400-600 W/mK while that for the reference is around $\sim$0.2 W/mK. This indicates orders of magnitude improvement in the effective thermal conductivity of electrodes with CNTs compared to that of commercially available technology [161]. It is important to note, there is a clear difference in the thermal properties in the CNTs coated with only silicon as compared to the other two samples. Based on our measured data, it is reasonable to state the overall improved thermal conductivity is due to the intrinsic thermal properties of CNTs which is above 2000 W/mK [93, 189, 87, 190]. However there is a clear difference
Figure 5.7: The cross plane temperature dependance of CNTs, along the CNTs axis coated with either amorphous silicon (a-Si), carbon or the combination of both are measured. The reference electrode, powder pressed with Si powder/carbon black allowing for relative comparision to the highly ordered CNT array coated with a-Si and carbon.

between the CNT/Si/C layers to the CNT/Si. It stands to reason the mechanism of the reduced thermal conductivity in the CNT/Si samples is a result of the diffusion of heat at the interface. The interface of the CNT and silicon layers diffuse heat well since the dominate contribution of heat in carbon materials [29] and semiconductor is a result to the contribution to acoustic phonons [37]. Here one can conclude heat diffusivity is enhanced in the CNT/Si/C nanowires verses CNT/Si nanowire arrays. In addition, these CNTs are
strongly coupled to the adjacent layers while the array of CNTs are highly oriented and extend over the whole length of the electrode. The weak temperature dependence of thermal conductivity, revealed in our measurements, is expected due to the multi-layer structures of the samples and the presence of non-crystalline materials across the axis of the CNT. The week $K(T)$ dependence will latter present a design advantage in extending the life of the battery since the electrode thermal properties are maintained at higher temperatures.

5.4.2 Electrical Resistivity Temperature Dependance of CNT Arrays

The ability for an electrode to conduct is an important aspect in the development of fast charge/discharge energy storage batteries [49, 160, 162, 191]. The temperature dependence of resistivity for the reference and three combinations of CNT materials have been investigated. The carbon nanotube electrodes have an electrical resistivity below 10 Ω-cm while the reference electrode is $\sim$900 Ω-cm. It is important to note, the measured resistivity here is the cross plane direction of the electrode which is parallel to the CNT axial length.

Temperature dependance of the CNTs show mostly metallic behavior. The weak temperature dependence of the CNT/Si and CNT/Si/C electrodes are characteristic of a disorder conductor [188]. A two probe method was motivated by the electrical configuration established in electrochemical battery design. It is important to note here, the resistivity of these sample includes contact resistance as a results of our two-probe method. However, the absolute resistivity values provide a clear understanding to conductive paths along the CNT array. The resistivity of the CNT are in agreement with an average resistivity $\sim$ 9.45 Ω-cm at RT [192, 193, 194, 195]. One should note the conductive properties along the axis of
Figure 5.8: Resistivity in the cross plane direction of the electrode with CNT coated with a-Si, carbon and the combinatin of both have been measured. The reference electrode has been shown to demonstrate a relative difference to that of the CNT based electrode.

the CNT/Si [196] are greater than CNT/Si/C samples [178]. These results provide insight data into the performance of nanostructured electrodes for energy storage and generation to improve fast charge/discharge rates or improved battery lifetimes times.
Chapter 6

Conclusions

Development of new energy generation and storage technologies are important for increasing the share of renewable energy sources and wider use of the plug-in electric vehicles. Thermoelectric energy conversion is suitable for the waste-heat recovery allowing for energy reuse. The limited use of thermoelectric generators is explained by low efficiency of the energy conversion defined by the thermoelectric figure of merit $ZT$. The factor that limits the scalability of energy storage in reversible electrochemical cells is high Ohmic losses, which degrade the battery performance.

In this dissertation, I investigated several innovative approaches for increasing the efficiency of the thermoelectric energy generation and battery storage via the use of nanstructured materials. It was theoretically predicted that strong quantum confinement of charge carriers and acoustic phonons can lead to drastic enhancement of $ZT$. I have used graphene-like mechanical exfoliation of $\text{Bi}_2\text{Te}_3$ and $\text{TiTe}_2$ to produce thin films with variable thickness. The exfoliated films were stacked together to form quasi-superlattices. Unlike
the epitaxially grown superlattices, the quasi-superlattice structures are characterized by nearly infinite potential barriers for electrons and phonons. Using the thermal and electrical measurements I have shown that ZT of such structures can be increased over a large temperature range via reduction of the phonon thermal conductivity. Specifically, I found a 77% increase in ZT values as compared to the reference bulk Bi2Te3 thermoelectric ingot.

I have also examined charge-density-wave effects in exfoliated TiTe2 films.

It has been previously shown that the core-shell nanostructure-based electrodes enable the combined strength of two or more materials to obtain enhanced energy-power densities in these batteries. The improvement is due reduction of the Ohmic effects. I investigated the thermal and electrical conductivities of the ultra-long vertically-aligned core-shell carbon nanotubes utilized in the Li-ion battery electrodes. The thermal conductivity, measured with the laser-flash technique, of the carbon nanotubes coated with amorphous silicon and carbon was in the range from 400 to 600 W/mK. The thermal conductivity of the highly aligned CNT/Si/C nanostructure electrodes was measured in the temperature range from 300 to 390 K. The thermal conductivity of the CNT-based battery electrodes is substantially higher than that of the reference battery electrodes. The electrical resistivity was shown to be two orders of magnitude lower than that of the conventional electrode. The results obtained for the Li-ion battery electrodes suggest that the use of nanostructured materials can substantially improve the thermal management of the batteries and their energy storage efficiency. The results of this dissertation are important for development of the new technologies for renewable energy generation and storage.
Bibliography


