Broadly defined synthesis and properties of phase change materials

Bokki Min

Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd

Part of the Chemical Engineering Commons

Recommended Citation

Min, Bokki, "Broadly defined synthesis and properties of phase change materials" (2018). Graduate Theses and Dissertations. 16415.
https://lib.dr.iastate.edu/etd/16415

This Thesis is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Broadly defined synthesis and properties of phase change materials

by

Bokki Min

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
Yue Wu, Major Professor
Zengyi Shao
Xinwei Wang

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

Copyright © Bokki Min, 2018. All rights reserved.
DEDICATION

In memory of

my mother In-sook Ryu
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>viii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>ix</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>x</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Transition Metal Dichalcogenides and Applications</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Synthesis and Properties of Nanomaterials</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Nanocomposite Solid Fabrication by Sintering</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Seebeck Effect</td>
<td>8</td>
</tr>
<tr>
<td>1.5 Structure and Properties of MXenes</td>
<td>9</td>
</tr>
<tr>
<td>CHAPTER 2 LARGE-SCALE SOLUTION-PHASE SYNTHESIS OF IRON TELLRIIDE AND P-N DIODE BEHAVIOR</td>
<td>12</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>12</td>
</tr>
<tr>
<td>2.2 Solution Synthesis of FeTe₂ Nanowires and Nanocomposite Fabrication</td>
<td>13</td>
</tr>
<tr>
<td>2.2.1 Materials</td>
<td>13</td>
</tr>
<tr>
<td>2.2.2 Synthesis of FeTe2 nanowires and nanocomposite disk fabrication</td>
<td>13</td>
</tr>
<tr>
<td>2.2.3 Result</td>
<td>15</td>
</tr>
<tr>
<td>2.2.4 Conclusion</td>
<td>25</td>
</tr>
</tbody>
</table>
CHAPTER 3   SYNTHESIS OF NANOSTRUCTURED TWO-DIMENSIONAL MXENE ................................................................. 26

3.1 Introduction .................................................................................................................................................. 26

3.2 Synthesis and characterization of Ti₃C₂ ........................................................................................................ 28

3.2.1 Materials .............................................................................................................................................. 28

3.2.2 Synthesis of Ti₃AlC₂ and Ti₃C₂Tx ......................................................................................................... 28

3.2.3 Result .................................................................................................................................................. 28

CHAPTER 4   FUTURE WORK ....................................................................................................................... 31

4.1 P-n diode behavior of FeTe₂ nanocomposite ......................................................................................... 31

4.2 Ti₃C₂Tx MXene ....................................................................................................................................... 31

REFERENCES ................................................................................................................................................. 32
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Crystal structure of MoS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Crystal structure of FeS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Top-down and bottom-up approach to synthesize nanomaterials</td>
<td>5</td>
</tr>
<tr>
<td>1.4</td>
<td>Schematic representation of spark plasma sintering</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>Schematic representation of Seebeck effect on semiconductors, ( \Delta V = V_{\text{hot}} - V_{\text{cold}} )</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>Scheme of FeTe&lt;sub&gt;2&lt;/sub&gt; nanostructure synthesis</td>
<td>14</td>
</tr>
<tr>
<td>2.2</td>
<td>Scheme of synthesis of FeTe&lt;sub&gt;2&lt;/sub&gt; (initial molar ratio Fe:Te=1:1) and FeTe&lt;sub&gt;2&lt;/sub&gt; (initial molar ratio Fe:Te=1:2).</td>
<td>15</td>
</tr>
<tr>
<td>2.3</td>
<td>XRD of as-synthesized (a) FeTe&lt;sub&gt;2&lt;/sub&gt; and (b) FeTe&lt;sub&gt;2&lt;/sub&gt;_&lt;sub&gt;2xFe&lt;/sub&gt;.</td>
<td>16</td>
</tr>
<tr>
<td>2.4</td>
<td>(a) TEM image of FeTe&lt;sub&gt;2&lt;/sub&gt;, (b) HRTEM image of FeTe&lt;sub&gt;2&lt;/sub&gt;, (c) FFT of FeTe&lt;sub&gt;2&lt;/sub&gt;, (d) TEM image of FeTe&lt;sub&gt;2&lt;/sub&gt;<em>&lt;sub&gt;2xFe&lt;/sub&gt;, (b) HRTEM image of FeTe&lt;sub&gt;2&lt;/sub&gt;</em>&lt;sub&gt;2xFe&lt;/sub&gt;. (c) FFT of FeTe&lt;sub&gt;2&lt;/sub&gt;_&lt;sub&gt;2xFe&lt;/sub&gt;</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>(a) Seebeck coefficient of FeTe&lt;sub&gt;2&lt;/sub&gt;_&lt;sub&gt;2xFe&lt;/sub&gt; (3-minute sintering), (b) Seebeck coefficient of FeTe&lt;sub&gt;2&lt;/sub&gt; (3-minute sintering), (c) Seebeck coefficient of FeTe&lt;sub&gt;2&lt;/sub&gt; (6-minute sintering), (d) Seebeck coefficient of FeTe&lt;sub&gt;2&lt;/sub&gt; (30-minute sintering), (e) Seebeck coefficient of FeTe&lt;sub&gt;2&lt;/sub&gt; (60-minute sintering), (f) Transition temperature of FeTe&lt;sub&gt;2&lt;/sub&gt; vs. sintering time.</td>
<td>18</td>
</tr>
<tr>
<td>2.6</td>
<td>(a) In-situ XRD of FeTe&lt;sub&gt;2&lt;/sub&gt; disk, (b) DSC result of FeTe&lt;sub&gt;2&lt;/sub&gt;_&lt;sub&gt;2xFe&lt;/sub&gt;. (c) DSC result of FeTe&lt;sub&gt;2&lt;/sub&gt;.</td>
<td>22</td>
</tr>
<tr>
<td>2.7</td>
<td>(a) Schematic illustration of thermally triggered p-n diode device. (b) I-V characteristic of FeTe&lt;sub&gt;2&lt;/sub&gt;-FeTe&lt;sub&gt;2&lt;/sub&gt;_&lt;sub&gt;2xFe&lt;/sub&gt;.</td>
<td>24</td>
</tr>
<tr>
<td>3.1</td>
<td>XRD of (a) Ti&lt;sub&gt;3&lt;/sub&gt;AlC&lt;sub&gt;2&lt;/sub&gt; and (b) Ti&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;T&lt;sub&gt;2&lt;/sub&gt;.</td>
<td>28</td>
</tr>
<tr>
<td>3.2</td>
<td>SEM image of Ti&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;T&lt;sub&gt;x&lt;/sub&gt;.</td>
<td>28</td>
</tr>
<tr>
<td>3.3</td>
<td>(a) SEM image of Ti&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;T&lt;sub&gt;x&lt;/sub&gt;, EDS mapping of (b) Ti element, (c) C element, (d) Al element, (e) F element, (f) O element.</td>
<td>29</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 3.1 Composition data from EDS analysis of Figure 3.3</td>
<td>29</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>S</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>electrical conductivity</td>
</tr>
<tr>
<td>$m_d^*$</td>
<td>Density of states effective mass</td>
</tr>
<tr>
<td>$n$</td>
<td>Carrier concentration</td>
</tr>
<tr>
<td>$h$</td>
<td>Reduced Planck’s constant</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>$e$</td>
<td>Charge on a proton</td>
</tr>
<tr>
<td>$A$</td>
<td>material dependent constant</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
</tbody>
</table>
I would like to express my deep gratitude to my advisor, Professor Yue Wu, who always supported and trusted me during my years at ISU. With his encouragement and motivation, I could successfully achieve accomplishments in research. I had limited knowledge and experience to perform research before his guidance. I much appreciate his consistent effort to train me as a valuable independent researcher.

I also want to thank all my group members including Dr. Biao Xu, Dr. Enzheng Shi, Huazhuang Zhu, Sungbum Hong, Zhe Li and Wei Zheng for their time and effort to train me. They were always eager to share their ideas and discuss about projects and their academic creativity always inspired and provided me with broader perspectives.

Lastly, I would like to thank my mother for supporting me emotionally and respect my decisions.
Phase change materials are currently used in numerous applications such as sensor, memory, detector, etc. due to change in properties when external stimuli are applied. Over the past few decades, nanostructured phase change materials have shown enhanced properties and characteristics compared to the conventional bulk phase change materials. Transition metal chalcogenides are reported to undergo thermally triggered phase transitions, yet there is still significant room for improvements for nanostructured FeTe$_2$. Also, two-dimensional MXenes are reported to have multiple phases due to change in the surface chemistry.

This thesis proposes solution phase synthesis and properties of FeTe$_2$ nanostructures with different Te vacancy concentrations and synthesis of nanostructured Ti$_3$C$_2$Tx MXenes. Te nanowires were first synthesized in the reactor with ethylene glycol solvent and Fe precursor was injected to form FeTe$_2$. The morphology changed from flakes to necklace structure as the concentration of iron precursor changed from the stoichiometric ratio to the iron-rich, respectively. These materials were washed and sintered into a nanocomposite disk using spark plasma sintering.

To study the properties of the FeTe$_2$ nanocomposite disk, Seebeck coefficient measurement was applied on the nanocomposite disk within certain temperature range. Phase transitions from p-type to n-type conduction were observed at phase transition temperatures. Phase transition temperature changed with sintering time and initial molar ratio between Fe and Te. The longer sintering time and excess Fe injection during solution phase synthesis resulted in higher Te vacancy in FeTe$_2$ and decrease in phase transition temperature. Two disks with different phase transition temperatures were integrated into one disk using spark
plasma sintering. I-V characteristic measurement was applied to the integrated disk while heating. As temperature increased, p-n junction was formed as one side of the disk with the lower phase transition temperature changed to n-type and the other side of the disk with the higher phase transition temperature still remained p-type. I-V characteristic measurements were conducted while heating and cooling and reversible switching behavior was observed.

MAX bulk disk was synthesized from TiH$_2$, Al, and TiC powders by spark plasma sintering. The disk was ground into fine powders and a 325-mesh sieve was used to ensure the particle sizes to be small for effective etching. To produce MXene, MAX powders were etched with concentrated hydrofluoric acid to remove Al between Ti$_3$C$_2$ layers.
CHAPTER I
INTRODUCTION

1.1 Transition Metal Dichalcogenides and Applications

Transition metal dichalcogenides indicates chemical compound consisting of two chalcogen anions and one transition metal cation. Although chalcogen is defined as any element in group 16 of the periodic table, sulfur, selenium, and tellurium generally are referred as chalcogens due to their chemical and technological importance. Transition metal dichalcogenides have attracted intense attention due to their interesting optical, magnetic, and electronic properties [1-3]. The structure of transition metal dichalcogenides can be categorized into two types: layered and non-layered structure. The layered materials consisting more than two third of transition metal dichalcogenides generally contain metal cations in group 4, 5, and 6 of the periodic table, and the non-layered materials generally contain metal cations in group 8, 9 and 10 of the periodic table [4].

Figure 1.1 Crystal structure of MoS$_2$. 

![Crystal structure of MoS$_2$.](image)
The layered materials have an anisotropic 2-dimensional atomic structure that two chalcogen anions and one transition metal cation are covalently bonded and form one layer, and each layer is weakly held by van der Waals forces as shown in Figure 1.1 [5]. MoS$_2$ has been intensively studied at various length scales from bulk to monolayers due to its thermal stability and resistance to oxidation [6,7]. The bulk MoS$_2$ is a good semiconducting material with an indirect bandgap of 1.29 eV [8]. The MoS$_2$ thin film with enhanced crystallinity has been obtained and employed for photovoltaic cell [9]. The considerable efforts have been devoted to developing numerous forms of nanostructured MoS$_2$ to take advantage of quantum confinement effects. Nanoclusters of MoS$_2$, deposited on the TiO$_2$ using in situ photoinduced fabrication, have been employed as photocatalysis due to strong absorption in visible light region [10]. The MoS$_2$ nanoplates offer large surface area and inter-layer gaps for intercalation, which makes it a promising candidate as an anode material for lithium battery [11]. Nanoparticles of MoS$_2$ have shown exceptional tribological characteristics for lubrication applications due to weak van der Waals bonds between molecular layers [12]. Monolayer or few layer MoS$_2$ have been successfully exfoliated mechanically and chemically [13, 14]. As the thickness of MoS$_2$ decreases below 100 nm the quantum confinement effects have more influence on the electronic structure and change the indirect bandgap into the direct bandgap of 1.9 eV according to calculations [15, 16]. Also, monolayer or few-layer transition metal dichalcogenides with Mo such as MoSe$_2$ and MoTe$_2$ have been explored due to interesting electronic structure and optical properties [17, 18].
A considerable amount of research has been conducted on non-layered transition metal dichalcogenides focusing on the change in optical, electronic, and magnetic properties due to compositional variations by doping or creating metal or chalcogen vacancies. FeS$_2$ consisting of earth-abundant elements is a semiconducting material with the bandgap of 0.95 eV [19] and have been employed for solar cell applications [20]. The sulfur and iron vacancies both on the surface and in the bulk can decrease the bandgap since they become acceptor-like and donor-like defects [21]. Co-doped FeS$_2$ nanospheres synthesized by a facile on-step solvothermal method have been employed as an anode material for sodium-ion battery [22]. FeS$_2$ bulk materials showed different semiconducting properties in carrier concentration, the type of charge carriers, resistivity, and Hall mobility based on the doping materials of nickel, cobalt and arsenic [23]. FeSe$_2$ materials have been employed for photovoltaic cells and anode materials for sodium ion battery due to its bandgap of 1.0 eV and good conductivity [24,25]. Cobalt-doped FeSe$_2$ was incorporated with graphene and
exhibited an outstanding electrochemical performance as an electrocatalyst for hydrogen evolution reactions [26].

1.2 Synthesis and Properties of Nanomaterials

Nanomaterials consists of the particles with the size from 1 nm to 100 nm or materials whose internal structure or surface structure have the size from 1 nm to 100 nm. The nanomaterials have their unique properties due to large specific area and quantum size effect. There are two main approaches to produce nanomaterials: top-down approach and bottom-up approach. The top-down approach starts with the large-scale materials with uniform structure and further reduce the dimension of the sample until nanostructures are fabricated. Lithography and etching process is widely used to manufacture the unique electronic nanoscale-circuits with high precision and performance [27]. Mechanical milling has been used to produce nanostructures but has the difficulty of controlling the uniformity, defects, and contamination [28]. The bottom-up approach, on the other hand, begins with atoms or molecules, which form clusters or seeds for further nucleation. The chemical or physical forces allow them to grow into self-assembled nanostructures with more controlled morphology, structure and chemical composition. The challenges for the bottom-up approaches are difficulty of large scale production and need for purification step to remove the contamination. The bottom-up approaches have been conducted in multiple phases such as vapor, liquid and solid. For vapor phase synthesis including flame synthesis, chemical vapor deposition, and atomic layer deposition, high external energy such as high voltage or heat is applied to the targets and atoms or molecules from the targets reacts and create nanostructures while they travel through the reactor. Liquid phase synthesis has been
developed due to low energy requirements and ease of controlling the morphology and structure of nanomaterials. The numerous nanomaterials including nanowires, nanospheres, nanotubes, etc. have been synthesized by chemical precipitation, hydrothermal method, sol-gel method, electrochemical deposition.

![Diagram of Top-down and bottom-up approach to synthesize nanomaterials.](image)

The properties of nanomaterials are much different from those of bulk materials due to their size, specific area, grain boundaries. As the dimension of the nanomaterials reaches to the de Broglie’s wavelength, the movements of charge carriers are spatially confined, and energies of charge carriers are quantized, which leads to formation of discrete electronic
energy level and changes electronic and optical properties [29, 30]. The gaps between adjacent energy levels increase with decreasing dimension of nanomaterials [31]. Extremely large surface area to volume ratio of nanomaterials facilitates the interactions or reactions with other atoms or molecules and enhance the performance of the electrochemical and catalytic devices. The countless number of grain boundaries in nanomaterial affects to the thermal and electrical properties due to enhanced phonon and photon scattering respectively, which greatly affect to the performance of thermoelectric materials [32].

1.3 Nanocomposite Solid Fabrication by Sintering

Sintering is the thermal treatment applied to a powder compact to increase its strength and integrity by heating to a temperature below its melting point. The nanomaterials synthesized in liquid phase must be washed multiple times for purification and dried completely into powder. The nanocomposite disk can be obtained by sintering the powder at proper temperature and pressure and it is important that nanostructures maintain their shape, size, and morphology without ripening or grain growth during sintering to take advantage of unique properties of nanostructures.

Hot pressing is the conventional technique that has been used to transform a powder to solid body by applying heat and pressure. The cost for operation is inexpensive but it requires long time since it only uses Joule’s heating and leads to Ostwald ripening. Even though initial powder has the nanostructure, the nanocomposite disk might not have or have slight difference in properties compared to bulk disk. Also, there could be multiple phases formed in the disk due to large internal temperature gradient generated by slow Joule’s heating [33]. Pressureless sintering is the process of compacting a powder into a solid bulk
material without pressure. This process enables the sample to maintain its original structure and porosity of a powder, but still requires long operation time.

Spark plasma sintering (SPS), also known as pulsed electric current sintering, has been developed to overcome disadvantages of damaging initial structure, grain growth, and lengthy operation time. SPS employs a pulsed direct electrical current and pressure under vacuum to compact the powder into solid body as shown in Figure 1.4. This process heats up and cools down the conductive powder at very high rates, which allows the nanostructure to
maintain its unique properties after densification by minimizing the temperature gradient within the powder.

1.4 Seebeck Effect

The Seebeck effect is a phenomenon that the temperature difference between each end of a semiconductor or conductor generates an electromotive force. The electrons and holes at the hot side have higher energy and travel to the cold side to reach thermodynamic equilibrium. The charge carrier difference between two ends creates the electrical potential difference. Even though the Seebeck effect was discovered using metals, semiconductors are more widely utilized to take advantage of Seebeck effect since the charge carriers must overcome the bandgap of semiconductors and the concentration difference of the charge carriers across temperature gradient is much larger than that of metals.

Figure 1.5. Schematic representation of Seebeck effect on semiconductors, $\Delta V = V_{\text{hot}} - V_{\text{cold}}$. 
The Seebeck coefficient is defined as the ratio of electrical potential difference to temperature difference.

$$S = \frac{\Delta V}{\Delta T} \quad (1)$$

The Seebeck coefficient can be explained by Mott formula [34].

$$S = \frac{\pi^2}{3} \left( \frac{k_B^2 T}{e} \right) \left( \frac{d \ln \sigma(E)}{d E} \right) \quad (2)$$

The Mott formula is generalized for semiconductors as the equation below [35].

$$S = \left( \frac{k_B^2 T}{e} \right) \left( \frac{E_F - E_c}{k_B T} + A \right) \quad (3)$$

The Seebeck coefficient can demonstrate the electronic structure of the material that the n-type semiconductors, in which their dominant charge carriers are electrons, have negative Seebeck coefficient and p-type semiconductors, in which dominant charge carriers are holes, have positive Seebeck coefficient at the given temperature. According to Mott formula, the Seebeck coefficient is dependent on temperature, effective mass, carrier concentration and band shape. The thermoelectric materials for power generation should maximize Seebeck effect and they are often doped with other metals to increase the carrier concentration for enhanced performance [36, 37].

1.5 Structure and Properties of MXenes

MXene is a new class of two-dimensional transition metal carbides and carbonitrides, which have been produced by selective etching A layers from MAX phases. MAX has the chemical formula of $M_{n+1}AX_n$ where M represents an early d-transition metal, A is mostly an element in group 13 or 14, X is carbon or nitrogen, and $n = 1, 2, \text{ or } 3$. M elements make stable covalent, ionic, metallic bonds with X elements generating two-dimensional layer
structure, whereas A elements are weakly bonded to other elements as shown in Figure 1.6.

After extracting A elements by etching, MXene has the chemical formula of $M_{n+1}X_nT_x$, where $T$ is a functional group, generally hydroxyl group, fluorine, or oxygen when hydrofluoric acid is used for etching [38].

![Crystal structure of Ti$_3$AlC$_2$.](image)

Figure 1.6 Crystal structure of Ti$_3$AlC$_2$.

Many MXene phases such as Ti$_3$C$_2$, Zr$_2$C, Nb$_2$C, etc. have been successfully synthesized by selective etching with hydrofluoric acid from MAX phase [39, 40]. Two different metals can occupy M sites randomly as $(Nb_{0.8}Ti_{0.2})_4C_3T_x$, and $(V_{0.5}Cr_{0.5})_3C_2T_x$ and in the ordered sandwich structures as Mo$_2$TiC$_2T_x$, and Mo$_2$Ti$_2$C$_3T_x$. The hydrofluoric acid has been widely used to etch A elements and produce MXenes. However, its hazardous properties have restricted the range of applications and other etchants such as hydrochloric acid and lithium fluoride salts have been suggested as relatively safer alternatives [41]. The etchants such as NH$_4$HF$_2$, NaHF$_2$ and KHF$_2$ not only extract A elements but also their cations...
intercalate between the MXene layers [42]. It is important to understand the effect of functional groups and the bare MXene phase without any functional groups has been synthesized by chemical vapor deposition for comparison [43]. Mono- or few-layer MXene has been obtained by intercalation and delamination of the multilayers. Transition metals are so reactive and organic materials intercalates into the gap between layers weakening the van der Waals forces between MXene layers which can be easily separated by sonication [44]. The M vacancies generated during etching and delamination process lead to different surface morphology and termination groups but do not change the metallic conductivity drastically [45]. In terms of cohesive energy and formation energy calculated by systematic simulation, Mxenes are very stable [46]. The theoretical study has proposed that the bare MXene is metallic but with the functional groups it can be a semiconductor [47].
CHAPTER 2
LARGE-SCALE SOLUTION-PHASE SYNTHESIS OF IRON TELLURIDE AND P-N DIODE

2.1 Introduction

The transition metal dichalcogenides containing iron such as FeSe$_2$, FeS$_2$, and FeTe$_2$ have been extensively studied due to abundance of iron and employed for the wide range of applications. FeTe$_2$ is a semiconducting material with the bandgap of 0.328 eV when its structure is marcasite according to the theoretical study [48]. Its narrow bandgap indicates that it can have n-type or p-type thermoelectric properties with proper doping or defect control. Although its performance as a thermoelectric material was not impressive, the phase transition from p-type to n-type conduction while heating has been observed [49].

Materials with switchable properties have been attracting much interest due to the promising applications such as memories, sensors, and detectors [50-54]. External stimuli such as light irradiation, electric field, temperature, and pressure can induce changes in their electronic, magnetic, optical and mechanical properties. Therefore, the ability to design and control the desired changes under external stimuli is the key prerequisite for the modern functional materials. Transition metal chalcogenides with non-stoichiometric ratios can easily switch their electrical properties from p-type (chalcogenides excess) to n-type (chalcogenides deficiency), which make them a suitable candidate for functional switching materials [54].

Recently, numerous transition metal chalcogenides exhibiting switching electronic properties under temperature stimulus have been reported. Tom Nilges et al reported Ag$_{10}$Te$_4$Br$_3$ can switch its electrical properties by a simple change of temperature due to high
silver mobility, a non-stoichiometric range, and an internal redox process [55]. A reversible p-n-p type conduction switching property in AgCuS material caused by phase transition has been reported by Kanishka Biswas’s group [56]. Thomas Palstra et al showed that the electrical property can be changed in marcasite FeSe$_{2\delta}$ by effect of vacancies [57]. However, the commercialization is hampered by low scalability and high cost [58, 59]. More importantly, it is difficult to control the transition temperature for switching electrical properties triggered by temperature.

This chapter demonstrates a low-cost and large-scale solution-phase synthesis of FeTe$_2$ using a robust, one-pot approach at low temperature and atmospheric pressure. We also demonstrate that the switching temperature can be tuned by changing the original precursor ratio. The defect concentration can be controlled by changing the sintering time, which makes it possible to control the switching temperature. Additionally, we developed a thermally triggered p-n diode device based on the above results.

2.2 Solution Synthesis of FeTe$_2$ Nanowires and Nanocomposite Fabrication

2.2.1 Materials

Tellurium dioxide (TeO$_2$, 99.99%) is purchased from Alfa Aesar. Polyvinylpyrrolidone (PVP, average 40,000 g/mol), potassium hydroxide (KOH, 99.99%), hydrazine (anhydrous, 98%), and iron chloride (FeCl$_3$, 97%) are purchased from Sigma-Aldrich. Hydrazine monohydrate (79%) was purchased from Tokyo Chemical Industry and ethylene glycol (EG) is purchased from VWR.
2.2.2 Synthesis of FeTe$_2$ nanowires and nanocomposite disk fabrication

For the synthesis of FeTe$_2$, 5.145 g of TeO$_2$, 14.625 g of KOH, and 450 mL of EG are added to 1 L three-neck flask with magnetic stirring initiated for continuous mixing. The reactor is heated to 70 °C and 9 g of PVP is added to the reactor slowly. The reactor is heated to 110 °C and 5.5 mL of hydrazine is rapidly injected into the reactor. The reaction is maintained at 110 °C for 1 hour under nitrogen gas protection using a Schlenk line. The reaction mechanism of the formation of Te nanowires is shown as below.

$$\text{TeO}_2 + 20\text{H}^- \rightarrow \text{H}_2\text{O} + \text{TeO}_2^{2-} \quad (4)$$

$$\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2^+ + 4\text{H}_2\text{O} + 4\text{e}^- \quad (5)$$

$$4\text{e}^- + 3\text{H}_2\text{O} + 3\text{TeO}_2^{2-} \rightarrow 6\text{OH}^- + \text{Te} \quad (6)$$

As the Te nanowires form, iron precursor solution is made in a nitrogen filled glove box. 2.6153 g of FeCl$_3$, and 50 mL of EG are added to a 100 mL beaker and heated to 80 °C. 26 mL of hydrazine is slowly added. The reactor is heated to 120 °C and the iron precursor solution is rapidly injected into the reactor. After four hours, the reactor is cooled at room temperature. The Figure 2.1 depicts the two-step synthesis of FeTe$_2$ nanostructures.

Figure 2.1 Scheme of FeTe$_2$ nanostructure synthesis.
The reaction products are centrifuged at 8800 rpm for three hours and washed with water by centrifuging two times at 8800 rpm for three hours and one hour. They are dispersed in ethanol using vortex mixer and ultra-sonication and transferred to 1 L three-neck flask. 80 mL of hydrazine monohydrate is injected into the flask and maintained at room temperature for 24 hours with vigorous magnetic stirring. The products are centrifuged at 8800 rpm for one hour and washed with ethanol by centrifuging two times at 8800 rpm for one hour each. The products are dried in vacuum for 36 hours and ground into powders with a mortar and pestle in the nitrogen filled glove box. The FeTe$_2$ powders then sintered into a disk by SPS for 3 min at 600 °C.

### 2.2.3 Results

![Figure 2.2 Scheme of synthesis of FeTe$_2$ (initial molar ratio or Fe:Te=1:1) and FeTe$_2$ (initial molar ratio of Fe:Te=1:2).](image)
The schematics illustration of the synthesis of iron telluride is shown in figure 2.2. Iron telluride morphology changed by adjusting the amount of iron precursor. The addition of iron precursor solution with the stoichiometric concentration (Fe:Te = 1:2) facilitates the formation of flake structure, while the addition of iron precursor solution with the doubled concentration (Fe:Te = 2:2 = 1:1) allows the necklace structure to be formed.

![Figure 2.3 XRD of as-synthesized (a) FeTe₂ and (b) FeTe₂₋₂xFe.](image)

The large-scale synthesis of FeTe₂ are first analyzed using X-ray diffraction (XRD). The result in Figure 2.3 (a) shows that the products of Fe:Te = 1:2 original ratio (which is denoted as FeTe₂) can be indexed as pure-phase FeTe₂ (red lines: JCPDS #14-0419). Figure 2.3 (b) is the XRD pattern of Fe:Te=1:1 ratio (which is denoted as FeTe₂₋₂xFe) and it can also be indexed as orthorhombic phase FeTe₂ (Red lines: JCPDS #14-0419). The XRD pattern indicates that there is no impurity in as-synthesized iron telluride.

The compositions of the products are further verified by transmission electron microscope (TEM). Figure 2.4 (a) and 2.4 (d) are the low-magnification TEM images of FeTe₂ and FeTe₂₋₂xFe, respectively. The FeTe₂ has flake structure while FeTe₂₋₂xFe shows
necklace structure. The only difference is the concentration of iron precursor solution, while all other experimental conditions remain constant. It is found that the concentration of iron precursor solution has a dramatic effect on the morphology of iron telluride. When the precursor solution with stoichiometric concentration of iron is added to the reactor, the diffusion rate of iron into Te nanowires is low and the internal strain of a crystal lattice is very high, which leads to the distortion or separation of nanowires into flakes. On the other hand, when the precursor solution with high iron concentration is added to the reactor, the diffusion rate of iron into Te nanowires is very high and the internal strain of a crystal lattice is low, which leads to preservation of nanowire structure.

Figure 2.4 (a) TEM image of FeTe\textsubscript{2}. (b) HRTEM image of FeTe\textsubscript{2}. (c) FFT of FeTe\textsubscript{2}. (d) TEM image of FeTe\textsubscript{2-x}Fe. (b) HRTEM image of FeTe\textsubscript{2-x}Fe. (c) FFT of FeTe\textsubscript{2-x}Fe.
Figure 2.5 (a) Seebeck coefficient of FeTe$_2$-2xFe (3-minute sintering). (b) Seebeck coefficient of FeTe$_2$ (3-minute sintering). (c) Seebeck coefficient of FeTe$_2$ (6-minute sintering). (d) Seebeck coefficient of FeTe$_2$ (30-minute sintering). (e) Seebeck coefficient of FeTe$_2$ (60-minute sintering). (f) Transition temperature of FeTe$_2$ vs. sintering time.
Figure 2.4 (b) and Figure 2.4 (c) are the high-resolution TEM (HRTEM) of FeTe$_2$ and its corresponding fast Fourier transform (FFT) image. The HRTEM of FeTe$_2$-2xFe and its corresponding FFT image are shown in Figure 2.4 (e) and Fig 2.4 (f). Both of FeTe$_2$ and FeTe$_2$-2xFe can be indexed as orthorhombic phase of FeTe$_2$ (space group is 58).

Large-scale (1 L per batch) and high yield (> 4 g per batch) synthesis of FeTe$_2$ enables sintering several 10 mm diameter FeTe$_2$ disk by SPS and investigating their electrical properties. The Seebeck coefficient decreases monotonically with temperature and switches from positive value (p-type) to negative value (n-type). Every sample is tested three times and this switching phenomenon is reproducible. The actual transition temperature for every cycle which is recorded by LSR-3 system software and the calculated average transition temperature is shown in the table in Figure 2.5 (a). Figure 2.5 (b) is the Seebeck coefficient of FeTe$_2$ and it also shows reproducible switching behavior for FeTe$_2$. Compared to FeTe$_2$-2xFe, FeTe$_2$ has a higher positive Seebeck coefficient value below 188.8 °C for FeTe$_2$-2xFe. At the range of 188.8 °C and 236.43 °C, FeTe$_2$ shows p-type behavior and FeTe$_2$-2xFe turns to n-type material. Both of FeTe$_2$ and FeTe$_2$-2xFe switch to n-type when the temperature is higher than 236.43 °C while the absolute Seebeck coefficient value of FeTe$_2$ is smaller than that of FeTe$_2$-2xFe.

A transition metal chalcogenide with excess chalcogenide, usually, shows p-type conduction while chalcogenide deficiency leads to n-type conduction. One possible reason is that, during temperature elevation, tellurium atoms out of position in iron telluride crystal will form poly telluride as the secondary phase and more tellurium vacancies are generated,
which switch the electrical conductivity from p-type to n-type. This mechanism can be expressed as an equation shown below using Kröger symbolism.

\[ Te'_Te \xrightarrow{\text{heat}} V'_Te + Te_i^x \]  

(7)

The subscript indicates lattice site while the superscription corresponds to electric charge of the relative to the site. According to electronegativity, iron has positive charge while tellurium keeps negative charge. On the left side of equation (7), one tellurium anion is sitting on a tellurium lattice site with negative charge. During heating, it decomposes into one vacancy in the tellurium lattice site with negative charge while tellurium atom is in the interstitial site with neutral charge. The Fermi energy is changed because of the change in volume of crystal during the formation of vacancy and the scattered electron waves at the point defects. Therefore, an increase in tellurium vacancies affects the valence state and change the electrical conductivity type. From macroscopic view, the equation can be written as following:

\[ FeTe_2 \xrightarrow{\text{heat}} FeTe_{2-\delta} + \delta Te \]  

(8)

where \( \delta \) indicates a very small number that will not affect the stoichiometric ratio. Every sample has reproducible result which means equation (7) and (8) are reversible within the temperature range of Seebeck coefficient measurements.

The Seebeck coefficient of FeTe\(_2\) with different sintering times of 3 minutes, 6 minute, 30 minutes, and 60 minutes are also showed in Figure 2.5 (c), Figure 2.5 (d), Figure 2.5 (e) respectively. Compared to the FeTe\(_2\) disk which is sintered for 3 minutes, FeTe\(_2\) with sinteiring time of 3 minutes, 6 minutes, 30 minutes and 60 minutes disks show lower transition temperatures. All the disks are tested three times and show reproducible switch
behaviour. The average phase transition temperatures from p-type to n-type for FeTe$_2$ with the sintering time of 6 minutes, 30 minutes and 60 minutes are 230.27 °C, 201.8 °C, and 195.8 °C respectively as shown in the inset tables of Figure 2.5 (c)-(e). Figure 2.5 (f) is the plot of average transition temperature vs. the logarithm of sintering time. There is a linear relationship between average transition temperature and logarithm of sintering time.

The possible reason of this phenomenon is that the sintering temperature is higher than the melting point of tellurium. All the disks are sintered at 600 °C and the melting point of pure tellurium is 445 °C while the melting point of iron is 1,538 °C. During sintering, the vacancy formation of Te is more vigorous than that of Fe. As shown in equation (9), tellurium will vaporize and be vacuumed by the pump. Therefore, Equation (9) is not reversible during sintering and the total concentration of tellurium vacancy is related to the sintering time.

$$FeTe_2 \xrightarrow{\text{heat}} FeTe_{2-\delta} + \delta Te \ (g) \quad (9)$$

Compared to the whole tellurium atoms, the concentration of tellurium vacancies is very small, and the laws of dilute solution can be used to calculate the relationship between sintering time and concentration of tellurium vacancies. The reaction rate and sample thickness are assumed to be constant, and the concentration of tellurium vacancies model can be expressed as following:

$$\frac{C(t) - C(t = 0)}{C_\infty - C(t = 0)} = 1 - e^{-\frac{kt}{L}} \quad (10)$$

Where t is the sintering time, k is the reaction rate and L is the sample thickness. $C(t)$ is the concentration of tellurium vacancies at time t. More tellurium vacancies are generated as the
sintering time increases and the transition temperature decreases as a result. The phase transition temperature of FeTe$_2$ are adjusted from 195.8 °C (60-minute sintering) to 236.43 °C (3-min sintering). More importantly, the transition temperature has a linear relationship with the logarithm of sintering time. In other words, the transition temperature can be controlled by changing the sintering time, which makes its switching behavior more useful.

Figure 2.6 (a) In-situ XRD of FeTe$_2$ disk. (b) DSC result of FeTe$_2$$_2$xFe. (c) DSC result of FeTe$_2$. 
To demonstrate the switching behavior, in-situ XRD of FeTe$_2$ is performed and is shown in Figure 2.6 (a). The FeTe$_2$ sample is sealed in the heating holder with Argon gas protection. The FeTe$_2$ peaks keep unchanged at all the temperature range until pure Te peaks (JCPDS #36-1452) appeared at 300 °C. The crystalline structure expands and the peak intensities shift right when temperature increases. The formation of secondary phase of tellurium crystallines at high temperature is due to the Te atoms that escapes their atomic position in iron telluride generating vacancies and changing the valence states of Fe atoms. The differential scanning calorimetry (DSC) result of FeTe$_2$ is shown in Figure 2.6 (b). There are no abrupt peaks in the temperature range from 70 °C to 350 °C, which means there is no phase change from solid to liquid during this temperature range. The DSC result of FeTe$_2$-2xFe also does not show phase change from 70 °C to 350 °C.

Materials with switching physical properties are good candidates for sensors and memories. However, usually the thermally triggered switching behaviors change gradually with temperature and the low switching speed hampers the applications for those materials [60]. Two iron telluride powders with different phase transition temperatures are sintered into one disk by SPS and the disk is fixed on the glass and connected to copper wires by silver paste. The glass substrate is placed on the hot plate and copper wires are connected to I-V measurement device and its I-V characteristic is measured as a function of temperature as depicted in Figure 2.7.
Figure 2.7 (a) Schematic illustration of thermally triggered p-n diode device. (b) I-V characteristic of FeTe$_2$-FeTe$_2$-2xFe.
Below the phase transition temperature of FeTe$_{2}$$_{2}$xFe, both FeTe$_{2}$ and FeTe$_{2}$$_{2}$xFe are p-type semiconducting materials and the I-V curve is straight lines which is regarded as the “ON” state. The I-V curve shows p-n diode behavior when the temperature reaches to the phase transition temperature of FeTe$_{2}$$_{2}$xFe and very low current is allowed to flow through the circuit, which is regarded as the “OFF” state. The crystalline structure of FeTe$_{2}$ and FeTe$_{2}$$_{2}$xFe are the same and there is no structural strain near the boundary, which makes the device stable. The thermally triggered p-n diode behavior with drastic increase of electrical resistance makes it a good candidate for thermal sensors.

2.2.4 Conclusions

In summary, a large-scale solution-phase method of FeTe$_{2}$ synthesis at low temperature and atmospheric pressure is developed. The phase transition temperature can be tuned by changing the iron concentration during the solution phase synthesis of nanowires. More importantly, the phase transition temperature has a linear relationship with the logarithm of sintering time, making it controllable by adjusting the sintering time. The secondary phase formation of tellurium confirmed by in-situ XRD and DSC measurement leads to the change in electronic property and induces p-n diode behavior. The thermally triggered p-n diode device indicates its potential application as a thermal sensor or thermal resistor.
CHAPTER 3
SYNTHESIS OF NANOSTRUCTURED TWO-DIMENSIONAL MXENE

3.1 Introduction

Since the discovery of the single-layer graphene obtained by mechanical exfoliation, two-dimensional materials have been extensively explored due to their unique physical properties originated from anisotropic transport of charge and heat. Two-dimensional materials in nanoscale have shown interesting and fascinating properties taking advantage of quantum confinement effect, and surface chemical modification. The electronic properties of nanostructured graphene can be tuned by creating defects and/or dopants. Both n-type and -type graphene has been created by nitrogen and boron doping respectively [61]. Also, the functional groups chemisorbed on graphene can greatly change the band structure [62]. Silicene and germanane that have similar structure as graphene have different bandgap values depending on the doping species [63, 64].

All the MXenes without functional groups and most MXenes with functional groups are metallic. However, some MXenes such as ScC$_2$, Ti$_2$C, Zr$_2$C and Hf$_2$C with specific functional groups have been suggested to become semiconducting with different bandgaps according to first-principles calculations [65]. The band structure calculation predicted that Ti$_3$C$_2$(OH)$_3$ and Ti$_3$C$_2$F$_3$ have a bandgap of 0.05 eV and 0.1 eV respectively [38]. However, the transition from a metal to a semiconductor by functionalization has not been observed through experiments.
This chapter demonstrates the synthesis and characterization of Ti$_3$C$_2$T$_x$. Ti$_3$C$_2$T$_x$ was produced by etching Ti$_3$AlC$_2$ with hydrofluoric acid and contained the functional group of OH, O, and F.

3.2 Synthesis and characterization of Ti$_3$C$_2$

3.2.1 Materials

Titanium carbide powder (98%) and hydrofluoric acid (49%) are purchased from Sigma Aldrich. Aluminum powder (99%) is purchased from Alfa Aesar.

3.2.2 Synthesis of Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$

0.645 g of TiH$_2$ powder, 0.363 g of Al powder, and 1.492 g of TiC powder are mixed well and sintered into a disk to synthesize Ti$_3$AlC$_2$ disk by using SPS at 1350 °C for 60 minutes. The disk is crushed and ground into fine powders for effective etching. The powder is then etched with hydrofluoric acid for 24 hours to produce Ti$_3$C$_2$T$_x$. The solution is washed once with water for 10 minutes and four times for 20 minutes by centrifuging at 8800 rpm to remove undesired products or impurities. After removing the supernatant, the sediment is dried under vacuum for 24 hours.

3.2.3 Result

Many combinations of reactants and heat treatment methods have been reported for synthesis of Ti$_3$AlC$_2$. N. Tzenov et al used the mixture of titanium, graphite and Al$_4$C$_3$ powders using hot pressing [66]. X. Wang et al used the mixture of titanium, graphite and titanium carbide using hot pressing [67]. Y. Zou et al used the mixture of titanium, Al$_4$C$_3$, and titanium carbide powders using SPS [68]. Although TiH$_2$ is much cheaper than Ti powders, Ti powders were used since TiH$_2$ needs long annealing time to get rid of hydrogen...
from TiH₂. SPS method provides the solution for this process by generating heat more effectively than the traditional methods.

In Figure 3.1 (a), XRD result is obtained to confirm the phases in the powder synthesized from TiH₂/Al/TiC. The peaks for Ti₃AlC₂, and TiC are present and the intensity of Ti₃AlC₂ peaks is much higher than other peaks, which indicates that the material is mainly composed of Ti₃AlC₂ phase. In Figure 3.1 (b), XRD result of Ti₃C₂ is obtained and no significant peak for impurity was found.

Figure 3.2 SEM image of Ti₃C₂Tₓ
After HF etching, Al elements that held Ti$_3$C$_2$ layers by metallic bonding are removed and layers are held by weak van der Waals interactions, which results in delamination or separation of layers as shown in Figure 3.2.

Figure 3.3 (a) SEM image of Ti$_3$C$_2$Tx, EDS mapping of (b) Ti element, (c) C element, (d) Al element, (e) F element, (f) O element.

Table 3.1 Composition data from EDS analysis of Figure 3.3.

<table>
<thead>
<tr>
<th></th>
<th>Wt%</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>5.59</td>
<td>16.17</td>
</tr>
<tr>
<td>O</td>
<td>3.66</td>
<td>7.93</td>
</tr>
<tr>
<td>F</td>
<td>8.68</td>
<td>15.86</td>
</tr>
<tr>
<td>Al</td>
<td>0.98</td>
<td>1.26</td>
</tr>
<tr>
<td>Ti</td>
<td>81.09</td>
<td>58.78</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
The exposed Ti atoms at the surface are very unstable and easily react to make bonds with fluorine, oxygen, and hydroxyl group spontaneously. Energy-dispersive X-ray spectroscopy (EDS) analysis of Ti$_3$C$_2$ powder is performed as shown in Figure 3.3. and Table 3.1 and confirms presence of fluorine and oxygen elements. The fluorine concentration is much higher than that of oxygen. Ti atoms react with fluorine during etching and with oxygen or hydroxyl group during etching and washing with DI water. The ratio between fluorine and oxygen can be controlled by emerging the powder in water. The longer the powder is in water, the more oxygen or hydroxyl group chemisorb on the Ti atoms.
CHAPTER 4

FUTURE WORK

4.1 P-n diode behavior of FeTe₂ nanocomposite

The FeTe₂-FeTe₂₂xFe disk showed p-n diode behavior but its I-V characteristic indicates low on-off ratio. The device should achieve much higher on-off ratio for industrial applications and high on-off ratio can be obtained by reducing the dimension of the device such as thin film. The major challenge of deposition of thin film is the formation of shunt path, which cause the short circuit. There are several factors such as the concentration of FeTe₂ solution, time of deposition, sintering temperature and time, etc. to be optimized to deposit uniform thin film with consistent thickness.

4.2 Ti₃C₂Tx MXene

The SEM/EDS analysis shown in Chapter 3 only provides the presence of fluorine and oxygen in the sample and do not offer the information how they are bonded to other elements. Raman spectroscopy, X-ray photoelectron spectroscopy, high-resolution TEM should be used to identify how the elements are bonded to each other. Incorporating all the information from those characterization techniques, the distribution of functional groups that are bonded with Ti atoms on the surface can be obtained. The techniques to generate different distribution of functional groups should be developed to demonstrate the relationship between the functional group and the electronical and electrochemical properties of MXenes.
REFERENCES


46. I. R. Shein, A. L. Ivanovskii, Graphene-like titanium carbides and nitrides Ti$_{n+1}$C$_n$, Ti$_{n+1}$N$_n$ (n = 1, 2, and 3) from de-intercalated MAX phases: First-principles probing of their structural, electronic properties and relative stability, *Computational Materials Science*, 2012, 65, 104-114.


