A Study of Energy Materials via Transmission Electron Microscopy

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A dissertation submitted to the Department of Physics, College of Natural Science and Mathematics in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in Physics

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University of Houston December 2021

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Dedication

I would like to simply dedicate this dissertation to my family, whose love and encouragement made my return to school, and ultimately this dissertation, possible. My Uncle Patrick, Aunt Alisa, my cousins, Norman Hofherr, Alexander Wang, and my father all gave me the support and confidence needed for this to become a reality. Especially to my mother who supported and inspired my love for science and nature as young as I can remember.

Acknowledgements

My time as a graduate student has been filled with a wide range of accomplishments, struggles, and emotions on more than one level. I feel so fortunate to have been working for Professor Shuo Chen who has been an incredibly stabilizing force throughout both the good and tough moments in the midst of some rather unusual times. Her wisdom, patience, and compassion, has been invaluable toward whatever success I may see now and will see in the future. The dedication she has shown me extends well beyond academics and research, as I always felt that I had someone personally in my corner to offer support and advice in any important matter both as a professional and as a friend. It has been so encouraging to know that my best interest has always been a sincere concern of hers. It is honestly difficult to put into words the gratitude I have toward her and toward the privilege of being in this position.

My committee members have all been important to my career at the University of Houston, both as graduate and an undergraduate student, being mentors to me in their own unique ways. Professor Rebecca Forrest was the first to welcome me into the Department of Physics as my advisor and has remained an inspiration to me since my first physics class that she instructed. Professor Donna Stokes was the instructor of my first advanced physics class and has always played a key support role for me from within the department. Professor Oomman Varghese instructed two of the most important class I've taken in regard to my research, and I will always be grateful that he convinced me to remain in his semiconductor physics class as a graduate student. Professor Zhifeng Ren and his terrific research group at TcSUH has provided me with opportunity and support that was absolutely crucial for my graduate work, and the experience was invaluable. Professor Jiming Bao provided resources to projects that I worked on even before I came to work for Professor Chen.

So many others have helped me along the way, such as Dr. Dezhi Wang who taught me basically everything I know about TEM, and was always there for friendly help and support. Jingying Sun, Jun Mao, and Shaowei Song all provided help and support at various stages during my research in the group. Also a special thanks to Luo Yu and Libo Wu for the opportunities to work with them and be a part of their terrific projects. I will always have a tremendous amount of gratitude for everyone mentioned here. Thank you everyone!

Abstract

This work recognizes the imperative need for green energy solutions in order to secure a clean and safe future for the planet. Transition from greenhouse producing fossil fuels can't happen overnight, as green energy technologies will have to be introduced into the global infrastructure in tiers according to their economic feasibility. Intermittent renewable sources like solar and wind are in need of a storable, transportable, and clean energy carrier to expand their contribution to the global energy supply. Hydrogen gas is the most promising candidate to play this role, as H₂ production and usage is as clean as the renewable sources themselves. Generation of H₂ and O₂ from water, or electrolysis, on industrial scales will require water-splitting catalysts to perform as efficiently as possible, so the design of novel materials to serve as these catalysts is an important field of research. Three interesting electrocatalysts are investigated via transmission electron microscopy to gain insights on their properties through their structure and composition. One involves a facile, ultrafast, and energy-inexpensive synthesis method to directly grow the active species on the substrate. Another uses a low-energy synthesis technique to modify and improve the layered double hydroxide structure, which is one of the more promising structures in the field. The last involves a core-shell structure that shows excellent potential especially in seawater splitting.

On a smaller tier, thermoelectric generators are more immediately assessable and can improve the energy efficiency of existing technologies by converting waste heat into useable electricity. Some of the most promising candidate materials are Mg₃Sb₂-based compounds. Understanding of charge carrier mobility is critical toward improving the power factor, which is needed to increase the output power density of devices. A precise understanding of the thermally activated mobility seen in these materials has not been achieved. This work investigates this phenomena via a microstructural comparison between samples with variation in their room-temperature conductivities. Interesting results are found involving crystalline bismuth segregations in Mg3.2Sb1.5Bi0.5Te0.01 samples that involve lower temperature synthesis conditions. This result could lead to a better understanding of low temperature mobility in this as well as other similar material systems.

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Chapter I Introduction

Transmission electron microscopy, having the ability to uncover a material's structure down to the atomic scale, is currently one of the most powerful and versatile analytical tools in the world of materials science. All of a material's properties can be linked to its micro, nano, and atomic structures in one way or another, and TEM gives the scientist an all-important eye into this environment – and seeing is believing. For this reason TEM will serve as an indispensable tool for the development of these materials and thus the advancement of green technologies. This dissertation recounts my TEM study of energy materials, specifically water-splitting electrocatalysts and the thermoelectric compound Mg₃Sb₂.

1.1 Toward a Low Carbon Future: Green Energy Technologies

The growing need for energy is a common factor for every nation on the planet regardless of their economic or social statuses. Global demand for energy has shown exponential growth in the past several decades, with an increase from 8,588.9 megatons of oil equivalent (Mtoe) in 1995 to 13,147.3 Mtoe in 2015 alone, and with no reason to believe the trend will not continue as such.(*1*) Energy supply will always be key to both developed and developing nations alike, where currently fossil fuels account for about 80% the worldwide need with renewable sources, such as solar, wind, tidal, hydroelectric, etc., provide the remaining 20%.(*1*) Although fossil fuel reserves seem to be adequate for the near future, inherent problems with them have become glaring issues which can no longer be ignored. First of all fossil fuels are not renewable, and a diminishing supply

will continually lead to difficulties in exploration and extraction. However, the more immediate concern is the production of climate changing greenhouse gasses that can't be avoided with the conversion of fossil fuels into usable energy. It is widely accepted in the scientific community that we are dangerously close to a runaway climate changing effect, inevitably leading to a host of irreversible environmental, ecological, and social crises.(*2*)

The climate change issue has forced scientists and engineers to research and develop technologies that can both meet the continuously growing energy demands while reducing CO₂ emissions. The most obvious way is to increase the contribution of renewable sources to the global supply. Perhaps the largest problem with renewable sources, particularly wind and solar, is that the power they provide is intermittent with no way to guarantee that peak demands will be met with peak production. Thus methods for large-scale energy storage must be developed where the energy carriers are dense, transportable, and clean. Battery technology will always play an important role in energy storage, but is impractical for storage and transport on the largest of scales. Chemical energy in the form of hydrogen gas, although with a low volumetric energy density, has a mass energy density more than double that of any commonly used fuel and can be stored and used at various scales. (3-5) H₂ storage when produced by electrolysis is considered the cleanest form of energy storage and has the ability to be transported long distances while even possibly using existing natural gas networks. (6, 7) Currently electrolysis is not the most cost effective means of production for H₂; hence this stage in the chain, from water to end user power, is an important area of research for scientists and engineers.(7)

Another important approach to address the energy problem to increase the efficiency by which energy is used and improve the way in which it is managed. Energy consumption in all sectors such as, industrial, commercial, residential, transportation, etc., have a large portion of their power released into the atmosphere as waste heat. It is common for industrial systems to capture and convert high temperature waste heat to useable energy via steam turbine systems, or Rankine and Stirling engines; this being practical because the amount of energy associated with the high temperatures.(8, 9) However, studies show that up to 60% of total waste heat energy in these settings occurs at low temperatures, ≤ 200 °C, being inappropriate for recovery by those types of systems.(8) A thermoelectric generator (TEG), a solid-state device that directly produces electrical current when exposed to a temperature gradient, could be optimized to operate quite well in this temperature range and thus could make a very meaningful impact toward improving the efficiency of energy usage by transforming waste heat into usable electricity.(9) Waste heat is by no means unique to industrial settings, as transportation of people and goods consume about 25% of the worlds energy production, where gasoline and diesel engine vehicles accounting for 75% of that and air travel another 12%.(10) Internal combustion engines are notoriously inefficient, where anywhere from 55% to 80% of fuel energy is lost as waste heat through engine coolant and exhaust.(9, 11) Automobile manufactures have already begun to design and implement TEGs for waste heat recovery in order to meet the increasingly stricter regulations for the reduction of CO₂ emissions.(9, 11, 12) The durability, versatility, and simplicity of TEGs make them the most practical devices to recover waste heat in internal and external combustion engines alike.

1.2 Electrolysis and Water Splitting

Passing an electrical current through a media in order to facilitate an electrochemical reaction, typically separating the compound media into its components, is known as electrolysis.



Fig. 1.1 Schematic of an alkaline electrolysis cell.(14)

Applying electrolysis to water will split the molecules in their components as oxygen and hydrogen gasses, which can then be collected and stored; where the global reaction quite simply is

$$2H_2O \rightarrow 2H_2 + O_2. \tag{1.1}$$

This occurs as two half-reactions at separate locations, namely the hydrogen evolution reaction (HER) taking place at the cathode, and the oxygen evolution reaction (OER) taking place at the anode.(13-15) The basic scheme of an alkaline electrolysis cell (AEC) is shown in Fig. 1.1.(14)

As the name suggests, the media between the electrodes is an alkaline solution, typically potassium hydroxide or sodium hydroxide, where the ionic species that propagate from the cathode

to the anode are hydroxyl ions (OH⁻). The electrolyte can be an acidic solution, or even a solid such as a polymer or an oxide ceramic, but the AEC will be the only cell discussed here.(14) The half-reactions that occur at their respective electrodes are

$$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$$
 and (1.2)

$$4OH^{-} \rightarrow 2H_2O + 4e^{-} + O_2, \qquad (1.3)$$

where Eqns. 1.2 and 1.3 are the HER at the cathode and the OER at the anode respectively.(13–15) The diaphragm in Fig 1.1 is a membrane that is permeable to the OH⁻ ions while ideally keeping the two gasses separated. Clearly if an applied electric potential is needed the reaction is thermodynamically uphill and nonspontaneous, where the total energy needed to split one mole of water into one mole of H₂ and one half mole of O₂ can be realized by the relation

$$\Delta_r H = \Delta_r G - T \Delta_r S , \qquad (1.4)$$

where $\Delta_r H$, $\Delta_r G$, and $\Delta_r S$ are the molar enthalpy, Gibbs energy, and entropy respectively, with *T* being the ambient temperature.(*14*, *15*) $T\Delta_r S$ is the heat energy supplied by the environment, and $\Delta_r G$ represents the electrical energy needed from an externally applied potential. The voltage needed to drive the reaction can be calculated from the Gibbs free energy by

$$U_{Rev} = \frac{\Delta_r G}{nF},\tag{1.5}$$

where U_{Rev} is commonly referred to as the reversible voltage, *n* is the number of electrons exchanged, and *F* is the Faraday constant (96,485 C mol⁻¹).(14, 15) At standard temperature and pressure we obtain the value

$$\Delta_r G^{\circ} = 237.22 \text{ kJ mol}^{-1} \rightarrow U_{Rev} = \frac{\Delta_r G^{\circ}}{2F} \approx 1.23 \text{ V}, \qquad (1.6)$$

which is the thermodynamically ideal voltage necessary to drive the reaction.(14, 15)

As always real systems are never ideal, the actual voltage needed to drive the reaction will be more than 1.23 V, where the additional voltage necessary to produce a desired amount of product is known as the overpotential. Minimizing this is critical toward achieving efficient electrolysis if large-scale H₂ production is to be realized and to make a real impact on the global energy supply. Sources of overpotential include ohmic resistances through the electrolyte and at electrode surfaces, and fluctuations in concentration of species in the electrolyte at the electrode surface relative to the bulk, mass transport limitations, and slow release of gas bubbles. However, a greater factor than these is easily the kinetic barriers inherent in the rate-limiting steps of the HER and, typically even more so, in OER.(*15*) Although the HER and OER are represented here as Eqns. 1.2 and 1.3, they each consist of smaller fundamental steps within their respective reaction pathways.(*14–16*) The role of an electrode to serve as a catalyst in order to facilitate the reactions and minimize overpotentials is crucial, and the research and development of these catalysts is of utmost importance.

Achieving low overpotentials is not the only necessary criteria for an electrocatalyst to make a widespread industrial impact; the materials used should be earth abundant and non-toxic while having cost-effective synthesis and fabrication methods. In fact the entire system, not just the catalyst materials, should be facile and relatively inexpensive. For instance the large scale use of an alkaline electrolyte is neither industrially attractive nor environmentally friendly. Platinum (Pt) for the HER and iridium oxide (IrO₂) for the OER were considered the best performing catalysts in fresh water until only within this decade, as the need to replace the rare elements with

less expensive materials for use in neutral water has been the focus of much research.(17-19)Electrolysis directly using seawater would be an ideal scenario as fresh water reserves would not be burdened, while H₂ producing installations could be easily combined with renewable electricity generation in coastal areas.(20-22) Seawater electrolysis presents its own set of problems such as excessive overpotentials facilitating the formation of hypochlorite that competes with the OER, instability of metal-containing catalysts due to the corrosive nature of seawater, formation of precipitates that can cover and poison the catalyst, and even bacteria and microbes naturally found in the media that inhibit performance.(20, 23)

Certain industrial demands for water-splitting catalysts regarding activity, efficiency, and stability must be met; wherein newly developed catalysts must be characterized and compared. The amount of overpotential required to achieve particular current densities, which is certainly a critical characterization, is only one of several electrochemical techniques used to study and compare performances, although none others are particularly discussed here. The focus of this dissertation regarding water-splitting catalysts will be microscopic structural characterizations via transmission electron microscopy (TEM). In addition to the various electrochemical characterizations, TEM analysis of newly developed materials in this field has become an invaluable tool toward gaining insights on the effectiveness of synthesis methods, design performance, and the guidance of new research.

1.3 Thermoelectricity

The field of thermoelectrics is about 200 years old, where Thomas Seebeck observed the deflection of a compass needle near a closed circuit of dissimilar metals with their junctions held



Fig. 1.2 Simple schematic of charge carrier distribution and resulting electric field within a TE material.(*26*)

at two separate temperatures. Oddly enough he attributed the observed voltage drop to an effect he termed as "thermomagnitism", where the term "thermoelectric" would not be coined until later.(24, 25) The phenomenon known as the "Seebeck effect" is the conversion of energy from heat flow into electrical energy as a material is subject to a temperature gradient. Charge carriers in a thermoelectric (TE) material, whether they be negatively charged electrons or positively charged holes, will diffuse from the hot side to the cold side creating an electric field and an associated electric potential. Fig. 1.2 shows a simple schematic of this.(26) The Seebeck effect is measured and mathematically defined by the ratio of the voltage it creates to the temperature gradient by

$$S = \frac{\Delta V}{T_H - T_C},\tag{1.7}$$

where S is the Seebeck coefficient, ΔV is the voltage difference measured along the temperature drop created by the Seebeck effect, and T_H and T_C are the hot and cold side temperatures respectively. About ten years after Seebeck's discovery, Jean Charles Peltier found the converse to Seebeck effect where passing a current through dissimilar metals would cause a temperature gradient at their junctions, and shortly after Heinrich Lenz was able to prove that this was indeed a thermoelectric effect and not an artifact of Joule heating.(24-26) This would come to be known as the Peltier effect, where the rate of heat energy absorbed or emitted at their respective junctions is given by

$$\dot{Q} = \Pi_{AB}I = (\Pi_B - \Pi_A)I, \qquad (1.8)$$

where \dot{Q} is the time derivative of heat energy, *I* is the electrical current, and Π_i is the Peltier coefficient of material *i*.(24, 27) The coefficients of the two effects are also related in general through the Kelvin relation

$$\Pi = ST \,. \tag{1.9}$$

Research into thermoelectrics remained little more than curiosity until the mid-21st century when it was discovered that doped semiconductors had much more prominent thermoelectric effects than previously studied materials. At that time most interest was in applications for refrigeration, and nearly every known semiconductor, semimetal, and alloy was studied for its thermoelectric properties. However, even the best performing materials had limited cooling ability and were only practical for niche applications.(*25*) The increased attention to the field of thermoelectrics gave new life for application of the TEG, being an attractive method of waste heat recovery due to growing energy and environmental concerns. A basic schematic of a TEG and a TE refrigerator, also known as a Peltier cooler is shown in Fig. 1.3.(*26*)



Fig. 1.3 (a) A TEG subject to a temperature gradient can supply electric power to a load. (b) A Peltier cooler with an applied voltage will create a temperature gradient. (a,b) The red and blue plates are hot and cold sides respectively, with I as the current direction.(*26*)

The efficiency of a TEG is proportional to the Carnot efficiency and is given by

$$\eta = \left(\frac{T_H - T_C}{T_H}\right) \frac{\sqrt{1 + Z\overline{T}} - 1}{\sqrt{1 + Z\overline{T}} + \frac{T_C}{T_H}},\tag{1.10}$$

where \overline{T} is the average temperature. Z is known as the figure of merit, which is how the performance of a thermoelectric material is characterized by, and is given as

$$Z = \frac{S^2 \sigma}{\kappa},\tag{1.11}$$

where σ and κ are the electrical and thermal conductivities respectively. The dimensionality of Z is T^{-1} , so the figure of merit is typically represented as the dimensionless quantity ZT. The numerator in Eqn. 1.11, $S^2\sigma$, is known as the power factor (PF), where σ is given in general by

$$\sigma = n\mu e , \qquad (1.12)$$

with *n* being the carrier concentration, μ the carrier mobility, and *e* the fundamental electric charge. The thermal conductivity is composed of both electrical and lattice components, specifically $\kappa = \kappa_e + \kappa_l$. κ_e is related to σ through the Wiedemann-Franz law by

$$\kappa_e = L\sigma T, \tag{1.13}$$

where L is Lorenz number.(24, 28)

From Eqns. 1.11, 1.12, and 1.13 we can see σ appears both in the numerator and the denominator for Z, which illustrates one of the many challenges inherent in raising the figure of merit. One reason why semiconductors are better TE materials than metals is that they have a lower Lorenz number, and thus the electrical conductivity of a semiconductor has less influence on the thermal conductivity than that of a metal. A good candidate TE material will also have an intrinsically low κ_l , and much study has been devoted to the search and analysis of structures conducive to low thermal transport. (29–31) Materials can be engineered to further reduce κ_l where techniques such as introducing various micro and nanostructures and all-scale hierarchical architectures to scatter phonons on various length scales have seen a lot of success over the recent decades.(32, 33) One of the most widely used methods for TE material synthesis consists of highenergy ball milling of constituent elements into a nanopowder solid solution. The powder is then hot pressed where it coalesces into a crystalline granular network, of which the grain boundaries (GBs) act as effective scattering centers for phonons, particularly at lower temperatures.(33) Synthesis methods can induce or control the formation of different defects on other scales, such as point defects (e.g vacancies, impurities, and interstitials), dislocations, and nanoscale precipitates which can also scatter phonons of other wavelengths leading to an overall reduction in κ_l .(29, 33, 34)

The study and application of thermally resistive structures is of clear importance toward raising *ZT*, however there is an amorphous limit to κ_l that has been closely approached by many materials, or even slightly exceeded is some cases.(*29*, *35*) Improvements to the PF must be made if TE materials are to realize a *ZT* > 3 and make an impact on at least some of the markets.(*36*) From Eqn, 1.11 we see the PF is comprised of the Seebeck coefficient and the conductivity, where *S* can be approximated by

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3},$$
 (1.14)

where k_B is Boltzmann's constant, h is Plank's constant, and m^* is the effective mass.(37) Again we see a conflicting terms within the PF, as $S \propto n^{-2/3}$, and more so as $m^* \propto \mu^{-1}$, thus n and μ must be carefully optimized in order for the PF to be maximized.(38) Many of the same micro and nanostructures responsible for low κ_l can also affect n and μ , thus a careful study of a material's structure and how it correlates with its TE properties is extremely important toward increasing its performance. TEM is an invaluable tool for the study of structure, as the work in this dissertation includes a TEM structural characterization of a magnesium antimonide (Mg₃Sb₂)-based compound to provide insights on the TE performance regarding its structural properties.

1.4 Magnesium Antimonide

Mg₃Sb₂-based compounds are semiconductors with the capacity to exhibit both n-type and p-type properties, although they typically have only been regarded as persistent p-type materials since the 1950's.(*39*) The search for high performing TE materials comprising of Earth-abundant elements has only just recently illuminated the potential for the n-type form in TEG and Peltier cooling applications.(40) Modifying the stoichiometry through alloying and doping while optimizing process conditions have allowed Mg₃Sb₂-based compounds to achieve near-room temperature performance comparable to that of state-of-the-art Bi₂Te₃-based compounds.(33, 39, 41-43) Thus Mg₃Sb₂ is an attractive candidate for both waste-heat recovery and cooling applications on a variety of commercial and industrial scales.

Mg₃Sb₂ belongs to a class of compounds with a general formulism of AB₂X₂, which are usually described as a Zintl phase. Typically in these compounds A would be an alkaline-earth element or divalent rare-earth element, B a transition metal or main-group element, and X coming from group 13, 14, or 15.(43) Mg₃Sb₂ is unique in this class such that Mg occupies both A and B within the formula unit, which can be denoted as Mg(1) and Mg(2) respectively. In general AB₂X₂ compounds with a trigonal crystal structure will form cationic layers of A^{δ +} intercalated with covalently bonded anionic [B₂X₂]^{δ -} layers.(43) Here Mg(1)²⁺ makes up the cation layer while [Mg(2)₂Sb₂]²⁻ makes the anionic layer. Fig. 1.4 is an illustration of Mg₃Sb₂ showing the trigonal crystal structure (space group $P\overline{3}m1$) and the ionic layers stacking perpendicular to the *c*-axis.(40)

The p-type character mentioned earlier is attributed to Mg(1) vacancies which act as acceptor sites consequently pinning the Fermi level into the valence band.(40) These vacancies have a low formation energy compared to other defects and must be mitigated to obtain an n-type character as well limiting the effect ionized-impurity scattering (IIS) on the charge carriers.(40–42, 44) A stoichiometric excess of Mg added during synthesis raises the chemical potential thereby controlling the Mg(1) vacancies to achieve the n-type character and enhance the low temperature carrier mobility in the process. Then the material can then be doped to further optimize the carrier concentration once the Mg(1) vacancies no longer dominate the electrical properties. In addition to excess Mg, Sb/Bi alloying is another ubiquitous strategy toward enhancing the TE properties.



Fig. 1.4 Structure of Mg₃Sb₂ with view from the a-b plane (left) showing the stacked ionic layers, and view from the c axis (right).(40)

Initially Bi substitution at Sb sites was most likely intended to induce phonon scattering centers by adding mass fluctuations in the covalent layer. However it has been shown through calculation and experiment that Bi alloying has beneficial electronic effects such as narrowing the bandgap and lowering the effective mass, both of which help increase conductivity especially at low temperatures.(*45*) TE materials prepared as so can be extremely sensitive to process conditions such as ball milling and hot-pressing parameters. In this work the structural characterizations via TEM were performed on Te doped Bi alloyed samples, Mg3.2Sb1.5Bi0.5Te0.01, where a significant increase in conductivity was achieved by only changing the hot-press temperature. Also studied was a Nb/Te co-doped sample, Mg3.1Nb0.1Sb1.5Bi0.5Te0.01, which has known to be an interesting case as well.

1.5 Conclusion

The transition from fossil fuels to clean energy alternatives will be an ongoing and arduous task that will not involve one simple solution, but rather a combination of technologies that can harvest the energy of our surroundings for us to use in a sustainable way. In an ideal world such technologies could be integrated into the world's energy supply and be developed and improved while placed in practice. Unfortunately, economic barriers demand that these technologies be mature enough and cost effective before implementation into industry at large enough scales to make a real impact and become cemented into our future. Hydrogen gas as a carrier for renewable energy transport and storage, and thermoelectrics to harvest waste heat and improve energy efficiency, both have tremendous potential toward being critical components of a green energy future. For this reason substantial efforts into the development of these technologies must not only be maintained but increased in order to secure their positions in the global energy network as soon as possible. At the heart of this research and development lies materials science, which is the conduit toward the success of these technologies. My contribution as a graduate student to the scientific community was aiding in the advancement of water-splitting electrocatalysts and thermoelectrics by studying the materials through transmission electron microscopy. This dissertation illustrates the significance and importance of TEM in the two fields and presents my understanding of the analysis techniques as well as the materials they were used to study. The structure of this document is briefly described by the following.

1.6 Dissertation Structure

The chapter succeeding this introduction presents the fundamentals of TEM, starting with the advantage the electron has over light in regards to microscopy. TEM hardware basics are explained and how the core components contribute to the functionality. The fundamentals of the operation modes and the associated imaging techniques employed in this work are outlined, with brief explanations of the physical concepts behind them. The chapter ends with a description of the sample preparations used herein. The third chapter consists of selected works from my collaborations with Prof. Ren's water-splitting catalysts group. Three unique experiments were chosen that I believe well illustrate the importance of TEM in that field of research, where the focus is primarily on effectiveness of synthesis strategy regarding structure and composition. An overview of the concepts behind the experimental approaches are presented to introduce the materials and the significance of the TEM analysis. The fourth chapter contains my TEM work of the microstructural direct comparison of Mg3.2Sb1.5Bi0.49Te0.01 thermoelectric materials that exhibit differing low/room-temperature conductivity behavior. The open question regarding the proper microscopic description behind a peculiar thermally activated conductivity is explained as the motivation behind the study. The importance of TEM sample preparation is displayed and interesting results that correlate with the materials' properties are disclosed. The final chapter summarizes the TEM work of the water-splitting catalysts and the work done on the Mg3.2Sb1.5Bi0.49Te0.01 thermoelectric material. A perspective is given regarding an *in-situ* TEM technique involving Kelvin probe microscopy. An explanation of the basic physical concept of the microscopy technique is provided as well as work that has been done with the *in-situ* setup.

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Chapter II Transmission Electron Microscopy

Systems designed to produce images of objects will consist of four basic elements in some form or another. First the object must be illuminated by some radiation, or be the source of radiation itself. Secondly, the object of interest scatters the radiation, where thirdly the radiation is collected and manipulated by apertures and lenses. Lastly it is projected in a useful way onto a detector of some sort. This is true for anything from the Hubble and radio telescopes, to the human eye, and most certainly microscopes. Electron microscopy, and in particular TEM, is no different in that respect, but clearly has its own set of physical principals by which it functions. An understanding of these principals is important toward properly interoperating data gained from the microscope, as this chapter outlines the fundamentals behind TEM and the associated techniques used in this work.

2.1 The Role of the Electron

In an optical microscope electromagnetic waves are manipulated by the ability of a lens to refract light due to the shape and refractive index of the lens's material. Enhancing the power of a lens system by increasing its ability to refract light becomes problematic as certain points in the design and construction are reached. However, lens construction is not the fundamental limitation of an optical system, but rather the ability of visible light to resolve, or distinguish, two separate objects. A focused object through a circular aperture will have a peak intensity in a center



Fig. 2.1 (a) Illustration of diffraction of light forms an Airy disc. The 0^{th} order maxima is at the center and is surrounded by concentric successive minima and maxima.¹ (b) An example of the separation of two resolvable objects limited by the position of the first minima aligning with the central maximum of the other.(2)

surrounded by concentric diffraction rings; this is known as the Airy disk, named after the work done by Sir George Airy.(I) Fig. 2.1(a) shows an illustration of the formation of an Airy disc due to diffraction. This diffraction essentially places a theoretical lower limit on an imaging system's ability to resolve two separate objects. This limit was both qualitatively and quantitatively described by Lord Rayleigh in the late 19^{th} century, as the Rayleigh criterion states that the minimum distance between two objects that are still resolved is reached when the central disk of the Airy pattern from one coincides with the first diffraction minimum of the other.(*1*) Fig. 2.1(b) shows this condition.(*2*) This minimum distance is realized by the relation

$$d_{min} = \frac{0.61\lambda}{NA_{ob}},\tag{2.1}$$

where λ is the wavelength of the radiation, and NA_{ob} is the numerical aperture. More specifically we have $NA_{ob} = n \sin \alpha$, where *n* is the refractive index and α is the semi-angle over which the objective can gather light from the object.(*1*, *3*) Even with ideal conditions light microscopes can only achieve $d_{min} \approx 200$ nm, and realistically that can't even be reached due to optical aberrations.

Perhaps the most important concept in electron microscopy is the wave-particle duality of the electron. First proposed by Nobel laureate Louis de Broglie where he stated the fundamental relation between a particle and its associated wavelength is given by

$$\lambda = \frac{h}{p},\tag{2.2}$$

where h is Plank's constant, and p is the momentum of the particle.(4) When an electron is traveling at relativistic speeds the wavelength is calculated by

$$\lambda = \frac{h}{\left[2m_0 eV\left(1 + \frac{eV}{2m_0c^2}\right)\right]^{\frac{1}{2}}},\tag{2.3}$$

where m_0 is the electron rest mass, eV is the kinetic energy, and c is the speed of light.(3) With an accelerating voltage of 200 kV, which is a very common energy used in TEM, the electron has a wavelength of 2.5 pm, being five orders of magnitude smaller than visible light. In fact electromagnetic radiation with comparable wavelengths would be gamma rays, which can be quite

destructive and unsuitable for microscopy. Visible light lenses utilize the refractive index in a transparent material in order to control the path of the wave and magnify an image, as electrons must be controlled in a similar way. Being charged particles, the trajectory of electrons are able to be manipulated by electric and magnetic fields, and a TEM employs electric fields to accelerate electrons and electromagnetic lenses to control their path. The following section describes a TEM's basic components and construction.

2.2 TEM Hardware Basics

Besides their very small wavelength, electrons are particularly well suited for imaging as they are relatively easy to generate and control. There must be a source where electrons are emitted and accelerated into a beam that is controlled by electromagnetic lenses and shaped to interact with the specimen. The post sample interaction contains the information from the specimen where transmitted electrons must be projected and magnified for imaging. A typical configuration of a TEM and its core components can be seen in Fig. 2.2.(5)

The electron source can be either a thermionic emission device, or a field emission device. In a thermionic device filament, typically made of tungsten or LaB₆, is heated to the point where electrons are sufficiently ejected. A field emission source operates at room temperature, although some are thermally assisted, where an electric potential is applied across a sharp tungsten tip. In the tip the electric field according to the relation $|\vec{E}| = V/r$, where r is the radius of the tip, increases substantially as r becomes small ($r < 0.1 \ \mu m$) thus lowering the work function and allowing electrons to tunnel from the tip.(3, 6) The beam produced by a cold cathode field emission device has a sharper energy distribution and a longer coherence length, but can be less stable than



Fig. 2.2 A simplified schematic of a TEM showing its core components of lens, aperture, and detector systems.(5)

the thermionic device. The source installed on the JEOL 2010F, the TEM used in this work, is a cold cathode field emission device. Accompanying the source is a configuration of one or more anodes which apply the accelerating potential, being responsible for the beam's energy and directing it into the TEM's illumination system. The source and the anodes together comprise the
electron gun. As the beam exits the gun it enters the first set of electromagnetic lenses known as the condensers. The electrons' interaction with the magnetic field induces a helical trajectory, but the field does no work on the electron, thus the lenses can control the size and shape of the beam without changing the energy or wavelength.(3) The condensers refine the beam by controlling its size and convergence and illuminate the specimen by producing a focused image of the source onto it with the desired magnification. The condenser aperture restricts the beam and limits the radiation through the illumination system, it also serves to reduce the effects of lens system's spherical aberrations.(5-7)

The objective lens collects the resulting interaction after the beam passes through the specimen. Typically considered the most important lens of the system as it produces the initial image and is responsible for the overall system resolution. The resolution of the TEM is not actually limited by the Rayleigh criterion described by Eqn. 2.1, but rather by aberrations in the lens systems. Highly advanced TEMs incorporate aberration corrections, but still do not approach the Rayleigh limit.(3, 7, 8) A diffraction pattern is formed at the back focal plane, where either the diffraction pattern or the image can be the object for intermediate lenses. Although not pictured in Fig. 2.2, an intermediate lens system after the objective prepares the beam for the projector lens, which is responsible for the final magnification and projecting the image onto the viewing screen or the CCD camera. There are two other devices to note that appear in Fig. 2.2, one being an annular detector, and the other being an X-ray detector. These will be further discussed shortly.



Fig. 2.3 The various types of interactions that an electron beam can have with a sample, showing different electron scattering modes as emission of photons.(3)

2.3 Imaging in the TEM

The ability to perceive an image relies solely on contrast, which is the difference in intensities of two adjacent areas. Contrast in beam intensities, either at the viewing screen or at a detector, will reflect variation within the sample according to how the incident beam interacts with the specimen. For this reason a basic understanding of this interaction is important toward acquiring and interpreting images and data. Fig. 2.3 schematically shows some examples of resulting interactions between an incident beam and a specimen.(*3*)

2.3.1 Diffraction Mode

In diffraction mode the current in the electromagnetic lenses are adjusted so that the object of the intermediate/projector lens system is the back focal plane of the objective lens where the diffraction pattern is formed. The pattern forms from elastic interactions with planes of a crystal, where the resulting interference pattern of electron waves is analogous to a two-dimensional continuous version of Young's double-slit experiment.(*3*, *9*) The points of high intensity result from constructive interference that conform to the Bragg condition,

$$n\lambda = 2d_{hkl}\sin\theta_B\,,\tag{2.4}$$

where *n* is an integer, λ is the wavelength of the electron, θ_B is the Bragg (scattering) angle, and d_{hkl} is the periodic spacing of the plane with Miller indices of *hkl*. The selected area aperture seen in Fig. 2.2 will be put in place in order to observe the diffraction pattern of a particular area, this is known as selected area electron diffraction (SAED). When SAED is performed on a single crystal that is well aligned with the incident beam, a plane of points of high intensity known as a spot pattern will be projected onto the viewing screen. This is actually a plane in the reciprocal lattice of the crystal, where each point represents a plane in the real lattice. Important analysis can be conducted on these patterns, as the zone axis and orientation of the observed crystal can be determined from the distance of these points from the central bright spot and the angles between them. This ability to identify and confirm crystalline phases is regarded as one of the most important roles of TEM in materials research.

Often materials are polycrystalline and composed of grains too small to be individually studied by SAED. This configuration will not produce a spot pattern, but rather a ring pattern that reflects the random orientation of the crystals. This still provides valuable information as the radius

of the ring corresponds to a particular lattice plane of the crystal. Analysis of ring patterns can be helpful when multiple species coexist within an area of interest, as the separate rings can easily be differentiated from each other, as opposed to the difficulty of distinguishing overlapping spot patterns.

2.3.2 Bright Field Imaging

Maybe the most basic and straight forward function of the TEM is bright field imaging, where the incident beam encompasses the specimen as a plane wave. As opposed to diffraction mode, the object of the intermediate/projector lens system is the image plane of the objective lens. The viewing area is largely illuminated with direct beam only, so areas of the specimen that significantly scatter electrons from the optical axis will produce low intensities. This is known as mass-thickness contrast, as areas in the specimen that are thicker or contain heavier elements will scatter electrons more.(*3*) This is particularly dominant at lower magnifications where relatively large variations in the specimen can be observed at once because of the wide viewing area. This is useful for scanning large particles while in search of smaller or more transparent features.

2.3.3 High Resolution TEM (HRTEM)

HRTEM is employed at higher magnifications where more information from the interaction between the incident beam and specimen is needed to provide contrast and obtain an image. Here phase contrast imaging plays the most important role, where interference between electron waves of varying phases produce the change in intensity necessary for contrast. This is only applicable when the specimen is sufficiently thin, as excessive scattering will create too much

interference and the image will be uninterpretable. HRTEM can identify crystalline structures as electron diffraction through lattice planes are imaged as fringe patterns that are directly related to those planes. The spacings of the fringe patterns can be measured on the micrograph according to the scale of the image to determine the corresponding plane spacing of the crystal. The imaging software is able to perform a Fourier transform of the lattice fringes, known as a diffractogram, which is effectively a calculated plane in the reciprocal lattice that corresponds to the orientation of the observed crystal. Analysis can be performed on a diffractogram in the same manner as a diffraction pattern with the ability to identify the lattice planes and the zone axis. This is an invaluable aspect of TEM especially regarding identification of separate species and phases within a particular sample.

2.3.4 Scanning TEM (STEM)

In STEM the incident beam does not broadly cover the specimen with a plane wave as in the previously mentioned imaging modes, but rather is converged onto the sample to a very small point, or probe, typically less than one nanometer in diameter. Deflector coils direct the beam in a raster scan pattern over the area of interest while maintaining the probe's orientation, thus the image forms serially pixel by pixel as opposed to parallel. The high intensity of the convergent beam typically produces more interaction with the sample than does the plane wave, making STEM very compatible with alternate imaging modes and analytical techniques. Although bright field imaging can be obtained with STEM, this work employs high angle annular dark field (HAADF) imaging in this mode. HAADF relies on electron beams elastically scattered at high angles, specifically around 50-200 mrad. The relative position of the detector used can be seen in



Fig. 2.4 A schematic showing the release of an X-ray as a higher-level electron fills a lower level emptied by an incident electron.

Fig. 2.2. The HAADF detector will receive a lot of scattered electrons from mass-thickness effects as opposed to bright field where these intensities are low, thus the high-low contrast areas are swapped between the two imaging modes. This is known as Z contrast, where the scattering cross section is proportional to Z^{α} ($\alpha \approx 1.7$ -2.0) with Z being the atomic number. So heavier elements show up with higher intensities than lighter elements.

Inelastic scattering is also important in STEM, in particular scattering events where incident electrons knock out an inner sell electron from an atom. A photon is released as an electron from an outer shell fills the emptied level, where the photon will be the energy of an X-ray that will be characteristic of that element. Fig. 2.4 shows a simplified illustration of this process. A detector in the TEM can collect these X-rays and assign the characteristic energies to their

respective elements, this is known as X-ray energy dispersive spectroscopy (EDS). EDS works very well in conjunction with HAADF as elemental concentrations can be mapped across an image, across a line scan, or just a spectrum at a single point. This is a very widely used technique and has become an invaluable standard in many areas of materials research.

2.4 TEM Sample Preparation

The success of a TEM experiment depends greatly on how a sample is prepared, and in some cases may be the most critical step. For an area of specimen to be observed it must be electron transparent, or at least to a certain degree, as different imaging and analysis techniques have their own allowable thickness thresholds. For HRTEM mass-thickness effects must be minimized and interference from diffraction must be the dominant form of contrast, where thicknesses of 50 nm or less are necessary.(*10*) Depending on the nature of the specimen this may or may be a significantly difficult task. On the other hand, HAADF relies high angle scattering intensities and will not be so sensitive to thicker preparations. Ideally it is best to gain as much information from a TEM experiment as possible, but particular questions that need to be answered will determine which types of analysis are most important, and thus will dictate preparation methods. Specimen preparations used in this work will be discussed here.

2.4.1 Particles on Holey Carbon Grids

It is common to take micro or nano scale particles suspended in a solvent and place them onto a TEM grid one drop at a time. The grids are 3 mm diameter metal mesh disks, where mesh openings can range from tens to hundreds of microns. A carbon film with holes, sized on the order of microns, is applied to the grid in order to support particles smaller than the mesh size. This is perhaps the simplest TEM preparation, and is very useful for studying particles grown on substrates that are incompatible with TEM observation. The catalysts studied in this work were grown on nickel foam, where some of the material was placed in a solvent and then were carefully ultrasonicated to preserve important features to be observed. The particles released into the solvent were then dropped onto the grid. Bulk TE materials were also prepared in this way, but with a less delicate process. A small piece of the material was placed in a mortar and pestle with the solvent and ground into a fine powder. With the heavy particles allowed to settle, drops from the top containing smaller particles could then be taken and placed on a grid.

2.4.2 Bulk Sample Preparation

Typically it is desirable to study a material as close to its intrinsic environment as possible, and this is often the case in bulk samples. A portion of the specimen must be made sufficiently thin while keeping the sample intact, which can be difficult process. For this work the surfaces were mechanically polished and thinned with increasing grains of sandpaper then finished with 1 µm diamond paste on a polishing cloth. The sample was thinned down to down to ≤ 30 µm while a ring style TEM grid was epoxied to a previously polished side. At this point one of two things happened, either the polishing continued until the thinned edge receded into the ring opening, or the a dimple was ground in the center of the ring creating an area of thickness of only a few micron. The dimple or the thin edge was then subject to argon ion beam milling to increase the thinned area. Much care must be taken with ion beam milling, as the milling can sputter amorphous material onto the sample or even destroy features of interest. So there is an important tradeoff that must be considered with the process. The ion beam milling was done with a Gatan PIPS II system, consisting of beams on the top and bottom of the sample at angles between 2.5-4.5° and energies between 2.5–4.0 keV. It is important to understand that any type of sample preparation can cause extrinsic artifacts and defects that don't represent the specimen's initial condition. It was found helpful in this work to employ different preparations on a single sample in order to learn as much as possible about the material.

2.5 Summary

TEM is the cornerstone of this research and the ability to effectively and accurately interpret data is crucial toward gaining insight of a material's properties. The purpose of this chapter was to convey a fundamental understanding behind the principals of electron microscopy, the key components of the TEM and their usage, imaging and analysis methods used in this work, and how samples were prepared for their study. The following chapters will describe the results and insights gained from applying these concepts to interesting materials in the fields of electrolysis and thermoelectrics.

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Chapter III TEM Analysis of Water-Splitting Catalysts

TEM has become a critical means for analysis in many fields of materials research, and the development of electrolytic catalyst are certainly no exception. The ability to study a material's structure on the micro, nano, and even atomic scale, to correlate structural attributes with a material's properties has given scientists and engineers new levels of understanding and has helped shape the direction of new research. For example, the role of electrocatalysts is to provide a medium to facilitate reactants to form intermedia states, so that the overall energy barrier of the reaction can be lowered, and the reaction kinetics can be improved. Thus, the structure, crystallinity, and composition, especially near the surface of electrocatalysts, are essential to understand their performances. This chapter contains selected works from my various collaborative efforts with Prof. Ren's water-splitting catalysts group. The works in the following sections have been previously published and are indicated as such.

3.1 Sulphur-Doped Nickel/Iron (Oxy)Hydroxide

The synthesis and experiment design of this work was done by Dr. Luo Yu of Prof. Ren's group, and can be found in the publication "Ultrafast room-temperature synthesis of porous S-doped Ni/Fe (oxy)hydroxide electrodes for oxygen evolution catalysis in seawater splitting"(*1*) As previously discussed the kinetics of OER and HER create an activation barrier above the ideal thermodynamic potential required to drive the reaction. The reaction intermediates in OER consist of multi-step electron transfer paths, being more complicated and require a larger overpotential

than HER.(2-4) This is typically a bottleneck in the electrolysis process and therefore significant attention has been devoted to developing increasingly efficient OER catalysts. Over the last several years bimetallic first row transmission-metal (oxy)hydroxides have seen a considerable amount of success, an even in some cases surpassed the benchmark rare-earth catalysts of iridium and ruthenium dioxides.(5-7) Nickel/iron-based (oxy)hydroxides (Ni/Fe-OOH) have shown to be among the most efficient OER catalysts while employing important performance enhancing strategies such as micro/nanoscale morphology designs to increase active surface area, defect engineering to modify electronic properties, and incorporating carbon materials to aid in charge transfer.(8-12) Despite the advances made in the OER performance most of the work done in this area suffers from complicated synthesis procedures that would cause large-scale production costly and impractical. The purpose of the work here was to introduce a scalable, facile, and inexpensive synthesis method for Ni/Fe-OOH electrodes as a promising means to realize the industrialization of seawater electrolysis. Here a one-step procedure was developed to fabricate Sulphur-doped Ni/Fe-OOH (S-Ni/Fe-OOH) catalysts on the surface of commercially available Ni foam at room temperature to provide a simplistic, cost effective, and energy efficient alternative to much of the work done on similar catalyst. The goal here is verify that the synthesis technique was able to achieve several important aspects of the material design. First it needed to be seen if the process was able to successfully grow the real active species of Ni/Fe-OOH in both a crystalline and amorphous environment. Secondly it was important to observe if the sulfur-doped structure achieved the porous morphology necessary to increase the active surface area exposing the active sites critical to electrocatalyst performance; thereby correlating the structure with adsorptiondesorption and X-ray photoelectron spectroscopy results.

3.1.1 TEM Analysis of S-Ni/Fe-OOH

Bright field images of the catalysts material can be seen in Fig. 3.1a,b. Fig. 3.1a shows a large variation in mass-thickness contrast throughout the entire particle. Fig 3.1b is a slightly higher magnification of the bottom boxed in section of 3.1a. The variation in contrast reveals a porous structure which is known to benefit OER by increasing surface area and aiding in the release of O_2 gas bubbles, which are two important factors in electrolysis.(12) The extensive porous network and pore size distribution seen in the images confirms data from scanning electron microscopy (SEM) and nitrogen adsorption-desorption tests. This data illustrates the effectiveness of the synthesis method's ability to modify the original surface of the Ni foam into a structure beneficial to OER. SAED was performed to observe the crystalline nature of the sample, where Fig. 3.1c shows several lattice planes identified in a ring diffraction pattern. The lattice planes (103), (102), (100), (002), and (110) from Ni(OH)₂ were all found within the selected area. STEM was performed, where Fig 3.1d shows HAADF image where the Z contrast highlights the porous structure quite well. Following below the HAADF image in Fig. 3.1d is the EDS elemental mapping. The maps show a relatively uniform distribution of the elements Ni, S, Fe, and O, as well as dark voids to further confirming the porous nature of the sample. HRTEM images were also obtained to study the structure in more detail, as seen in Fig. 3.2. The HRTEM shows lattice fringe patterns representing small randomly oriented crystal structures being consistent with SAED. The (001) lattice plane of Ni(OH)₂ in both Figs. 3.2a,b, where the (002) of NiOOH was also detected in 3.2b. The groups of crystals are interrupted by areas of amorphous material, which



Fig. 3.1 (a) Bright field image of a S-Ni/Fe-OOH particle on top of holey carbon film. (b) A higher magnification from the dashed box in (a). The mass-thickness contrast in (a,b) revealing porosity of the catalyst material. (c) SAED pattern with planes (103), (102), (100), (002), and (110) of Ni(OH)₂. (d) HAAFD image and EDS map of a particle showing uniform elemental distribution and further revealing pores.



Fig. 3.2 HRTEM of S-Ni/Fe-OOH. (a) Sample portion identifying (001) lattice plane of Ni(OH)₂, among other crystalline features, accompanied by amorphous areas. (b) Similar to (a) but with the NiOOH species identified.

seem to be plentiful in the sample. This is thought to increase the amount of active sites and benefit OER performance.(*13*) Plenty of Fe was found in the EDS data, but was not detected in crystalline form in the HRTEM or SAED, at least in the area studied here. X-ray diffraction data did show a peak that corresponded to FeOOH, but with an intensity very low compared to the other crystalline species. The rarity of the crystalline phases of FeOOH and NiOOH could mean that the two species were mostly in amorphous form. Also this could suggest that the two species largely formed oxidation of Ni/Fe(OH)₂ during the OER process, which is consistent with pre and post-OER X-ray photoelectron spectroscopy

3.2 Boron Modified Cobalt Iron Layered Double Hydroxides (B-Co₂Fe LDH)

The synthesis and experiment design of this work was done by Libo Wu of Prof. Ren's group, and can be found in the publication "Boron-modified cobalt iron layered double hydroxides for high efficiency seawater oxidation"(14). Among the leading candidates for water-splitting anodes are layered double hydroxides (LDHs), which are attractive because of their high OER activity and composition versatility.(15, 16) Put simply, LDHs are metal cation layers between layers of hydroxide anions, where these stacks are separated by charge compensating interlayer anions, among other neutral molecules such as water. (16–18) Earlier work with anodes fabricated from powder-based LDHs adhered to substrates suffered from poor conductivity and durability.(16, 19, 20) Hence there was a clear need for research focused on self-supporting LDH structures if their promising OER properties were to be realized in a practical device. Excellent work has been done in this area where direct growth of self-supporting LDH structures on highly conductive substrates, enhancing OER performance attributed to increased electron mobility between the LDH and substrate, larger surface areas to expose active sites, and surfaces more conducive to the release of O_2 bubbles.(20-24). Despite these advances, most bi- and trimetallic LDH catalysts suffer from fabrication constraints, as they consist of complex and energyexpensive hydrothermal synthesis techniques under high pressure that would be unattractive for large scale commercial/industrial production. One objective of this work was to address this issue by achieving a self-supported structure via a facile synthesis technique involving a two-step method under low temperature and being open to the atmosphere. Also, structurally amorphous catalysts have gained attention for their advances in OER performance, which can be attributed to a large amount of percolation paths and increased ion mobility.(25-27) More specifically boronbased amorphous catalysts have seen considerable success in showing high activities.(28-30)

Another objective here is to synthesize a Co/Fe-based LDH and modify its hierarchical nanosheetnanoflake structure with boron to exploit the benefits of a partially amorphous system. The purpose of the following TEM analysis was to verify the effectiveness of this unique synthesis strategy. Specifically, if the low-cost and scalable technique successfully grew the LDH structure by observing the morphology and crystallinity. Also the effect of the boron modification needed to be verified by looking for structural changes and dopant uniformity.

3.2.1 TEM Analysis of B-Co₂Fe LDH

TEM analysis was performed both before and after boron modification to provide detail of the structural evolution due to the process. Fig 3.3a is a low magnification bright field image of Co₂Fe LDH precursor, before boron modification. The nanosheet is largely electron transparent and with mass-thickness contrast revealing nanoflake decorations on the edge. Fig. 3.3b is a bright field image of a boron modified specimen showing a higher degree of contrast within the sample due to the creation of porous networks. The entire particle is highly decorated with nanoflakes, which in combination with the high porosity significantly increased the active surface area. Fig. 3.3c is a SAED pattern of the nanosheet before boron modification, where the (110), (107), and the (105) planes were identified. The faint rings accompanied by bright spots indicate that the specimen exhibited a high degree of crystallinity. Comparing this with the SAED pattern of the boron modified sample (Fig. 3.3d) we see the discrete bright spots are not present, but rather shows well-defined rings that are indicative of a large amount of defects in the crystals. The cloudy area inside the inner-most ring is a signature of amorphous material, in which the introduction of was



Fig. 3.3 (a) Bright field TEM of Co₂Fe LDH precursor. (b) High magnification Bright field TEM of B-Co₂Fe LDH. (c) Diffraction pattern of Co₂Fe LDH precursor. (d) Diffraction pattern of B-Co₂Fe LDH. (c,d) The scale bars are 2 nm⁻¹.



Fig. 3.4 (a) HRTEM micrograph of specimen before boron modification, composed of overlapping fringe patterns across the area. (b) HRTEM of boron modified sample, showing lattice structures interrupted by amorphous material.

one of the intentions of the synthesis method. HRTEM was performed to study the structure in more detail. Fig. 3.4a is an HRTEM micrograph of the specimen before boron modification. The structure is widely composed of dense crystallites, where a majority of the interior consists of overlapping fringe patterns resulting in moiré effects. Fig. 3.4b shows the HRTEM of the boron modified sample. Lattice structure is still easily recognized in the area, however the crystallinity is interrupted by amorphous material, being consistent with the SAED results. STEM was performed where a HAADF image was acquired with accompanied EDS elemental maps (Fig. 3.5). The HAADF image further illustrates the porosity of the B-Co₂Fe LDH, and the elemental maps show the uniform distribution of boron in the sample. This uniformity is important, as tests show that boron modification provides benefits such as enhancing conductivity and corrosion resistance in seawater electrolysis.



Fig. 3.5. STEM HAADF of B-Co₂Fe LDH and corresponding EDS mapping of the elements of interest.

3.3 Cobalt Phosphide Iron Oxyhydroxide Core-Shell Structure (CoP_x@FeOOH)

In addition to observation of homogeneous morphology, crystallinity, or random distribution of compounds in a material, TEM also provides direct evidence of specially designed nanomaterials, for example core-shell structures. The synthesis and experiment design of this work was done by Libo Wu of Prof. Ren's group, and can be found in the publication "Rational design

of core-shell-structured CoP_x@FeOOH for efficient seawater electrolysis".(31) Significant strides have been made toward the development noble-metal-free electrocatalysts, where the importance of surface engineering and structure can't be overstated. Core-shell structures, composites composed of an inner and outer material, can possess several means by which they increase catalytic efficiencies.(32) The composites can accommodate synergistic effects between different active species, helping to promote HER and OER kinetics.(33, 34) The interaction between the core and shell can include strain effects that modify the interfacial electronic configuration causing adsorption energies to be more compatible with reaction intermediates. (35, 36) Pristine catalysts that suffer from poor electron transfer can perform better as a composite with a suitable material where the overall charge transfer and series resistances are lowered. (22, 31, 32, 37-40) Along with these advantages that specifically address kinetics, there are other attributes that are very attractive for commercial and industrial applications. Durability is typically improved within these structures, which could satisfy industrial requirements for long-term use. Core-shell structures can have relatively large surface areas that significantly increase the amount of exposed active sites, which does not only benefit efficiency at high currents but can also improve catalyst longevity in natural seawater conditions, keeping active sites from becoming poisoned by contaminates(14, 31, 41-43). A shell can also be engineered to protect a vulnerable core material and increase its ability to resist corrosion in harsh seawater environments. Improvements in kinetics to keep overpotentials below 480 mV, which is the onset of chlorine evolution, along with improved durability and corrosion resistance make core-shell structured catalysts attractive candidates for large-scale industrial H₂ production. The TEM work here aims to study this promising nanomaterial by first understanding the structure of the core material and observe the state of the phosphorous-rich CoP_x and look for evidence of the material's durability. Second the ability of the

electrodeposition to fabricate a shell structure that can utilize the synergistic effects of combining the CoP_x and the FeOOH as well as producing a high surface area with both a crystalline and amorphous environment.

3.3.1 TEM Analysis of CoPx@FeOOH

The synthesis begins with a $Co(OH)_2$ nanowire mesh grown on commercially available Ni foam, where subsequent phosphidation was performed on the $Co(OH)_2$ precursor to synthesize the CoP_x nanowire mesh. This, as the core material of CoP_x @FeOOH, was first inspected by TEM (Fig. 3.6). The low magnification bright-field image in Fig. 3.6a shows a well-defined network of interwoven CoP_x nanowires. This mesh structure provides the core with mechanical durability on the macro scale and would be beneficial toward a practical device. Fig 3.6b is a higher magnification bright-field image showing individual nanowires with diameters less than 100 nm. The contrast within the wires clearly show significant variation of mass-thickness which was further investigated with HRTEM (Fig. 3.6c). The micrograph was taken in an area where the variation occurs on the nanometer scale, where analysis of the fringe patterns can be seen in the expanded view (Fig. 3.6d). The lighter area was determined to be the (201) lattice plane of the CoP species, where the (210) lattice plane of CoP₂ was found in the darker area, as the contrast is deemed to be the intimate coexistence of the two species within the heterogeneous PO_x nanowire. STEM was also employed so that EDS could be performed, where Fig. 3.7 is the HAADF image and the accompanying elemental maps. It is clearly seen that Co and P are well distributed throughout the nanowires.



Fig. 3.6 TEM of CoP_x (a) Low magnification bright-field image showing the nanowires in a woven mesh structure. (b) High magnification bright-field image showing contrast within the nanowires. (c) HRTEM showing lattice structure among the variations in contrast. (d) Expanded view of (c) with separate species of CoP and CoP₂ identified by their lattice fringe patterns.



Fig. 3.7 HAADF image of CoP_x nanowires and the corresponding EDS elemental maps showing the uniform distribution of Co and P.

FeOOH was electrodeposited onto the CoP_x to create a porous shell around the nanowire mesh, thus creating the core-shell structured CoPx@FeOOH, where TEM results from this structure are seen Fig. 3.8. Fig 3.8a is a high-magnification bright-field image of a section of nanowires protruding from the mesh. The surface of the nanowires have clearly been modified as they appear much rougher than the comparatively smooth surface seen in Fig. 3.6b. The texture of the surface confirms the porous nature of the surface and would be responsible for increasing the active surface area. SAED was performed on a portion of the nanowire to detect phases within the sore-shell structure, as seen in Fig 3.8b. Rings labeled "B" and "D" were measured as the (200) and (111) lattice planes of CoP respectively, rings "A" and "C" were identified as the (032) and (120) planes of FeOOH respectively, and ring "E" was detected as the ($\overline{102}$) plane of CoP₂. This was a good indication that the polycrystalline CoP_x core was still intact after the electrodeposition process. The cloudy region in the center of the SAED ring pattern indicates a significant presence of amorphous material, which can benefit OER and HER as discussed earlier. A more detailed study of the structure was enacted through HRTEM of the boundary region between the core and the shell (Fig 3.8c). The boundary can be identified by the sharp change in contrast in the bottom-



Fig. 3.8 TEM of CoP_x@FeOOH (a) High magnification bright-field image of a core-shell nanowire cluster. (b) SAED ring pattern where identified species are: A – FeOOH (032); B – CoP (200); C – FeOOH (120); D – CoP (111); E – CoP₂ (102). (c) HRTEM near the core-shell boundary with identified (111) lattice plane of FeOOH. (d) Expanded view of boxed in area of (c) where both (111) and (410) lattice planes of FeOOH are identified.

left corner of the micrograph. Although the core area was too thick to see any lattice structure, fringe patterns from FeOOH crystal structures were detected in the shell region. The (111) lattice plane of FeOOH was measured in a region close to the boundary in Fig. 3.8c, as well as in the expanded view (Fig. 3.8d). The (410) lattice plane was also detected and shown in the expanded view. Notice in Fig. 3.8c that the lattice structure largely remains close to the core-shell boundary, and lessens further away from the core. This seemingly amorphous region along the outer edge of the shell structure is in agreement with the SAED pattern. Fig. 3.8d is an expanded view of the boxed in area of Fig. 3.8c, with the (111) and (410) lattice planes of FeOOH which further illustrates the intimate contact between the CoP_x-core structure and the FeOOH-shell crystals. To further evaluate the electrodeposition synthesis STEM and EDS were carried out to determine the elemental distribution. Fig. 3.9 shows the HAADF image and the corresponding elemental maps. The definition of the nanowire core structure is found only in the Co and P elemental maps, while the Fe and O maps more broadly cover the region. This is also good evidence regarding the coreshell structure and the effectiveness of the synthesis technique.

3.4 Conclusion

The development and advancement of electrolytic catalysts is an extremely important field of green-energy materials research, and the analysis in the projects described above well illustrate the importance of TEM. For the sulphur-doped nickel/iron (oxy)hydroxide catalyst it was critical to show that a low cost and easily-scalable synthesis technique could adequately produce the necessary structural elements responsible for high OER performance. The TEM analysis showed the catalyst's porous structure on various scales, as well as crystalline and amorphous environment



Fig. 3.9 HAADF of CoP_x @FeOOH and corresponding elemental maps showing the FeOOH shell broadly covering the CoP_x cores.

of the active species to produce a synergistic working environment while providing large surface areas to achieve efficient OER performance, even in difficult natural seawater conditions. For these reasons it can be concluded that the energy efficient process was a promising and successful synthesis technique. For the B-Co₂Fe LDH two stages of TEM analyses were employed to provide direct evidence of the effectiveness of the low energy and facile synthesis, as well as the boron modification, on the widely explored LDH system. The analysis was able to explicitly show the ability of the low-temperature and scalable synthesis technique to produce the LDH structure. Also, the partially amorphous transformation the of the Co₂Fe LDH precursor due to the boron modification was clearly evident through bright-field images, HRTEM and SAED. The work not only introduces a stable and efficient candidate for seawater electrolysis, but also provides a unique fabrication approach to improve LDH-based catalysts.

The work on CoP_x@FeOOH also consisted of two separate TEM experiments to examine the catalyst at different stages of the synthesis. A Co(OH)₂ nanowire mesh successfully underwent phosphidation to create the robust CoP_x core with the nanowire structure well intact. The STEM and EDS showed a uniform distribution of Co and P while HRTEM was able to detect crystalline species of both CoP and CoP₂. This could be one reason why CoP_x served more purpose than only the core material for CoP_x@FeOOH as it was found to be an efficient HER catalyst in alkaline seawater. TEM analysis on the complete core-shell structure confirmed the successful electrodeposition of the FeOOH onto the CoP_x core. Bight-field images clearly showed a thin shell material covering the thicker nanowire core. SAED showed crystalline species of CoP, CoP₂ and FeOOH, as well as the presence of amorphous material. This was further confirmed by a HRTEM micrograph of the core-shell boundary, as crystalline FeOOH was detected near the boundary and apparent amorphous material detected away from the boundary. The EDS data provided even more evidence of the successful core-shell synthesis, as Fe and O was found to cover an entire cluster of nanowires while Co and P elemental maps strictly defined the nanowire cores. The combined analysis helped to indicate that this synthesis technique could be an effective universal method for

the future development of catalysts for seawater electrolysis.

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Chapter IV

TEM Investigation of Mg₃Sb₂-Based Compounds Exhibiting Thermally Activated Mobility

4.1 Introduction

In addition to observation of particulate samples, TEM is widely used to characterize bulk materials. An example is thermoelectric composite materials, where atomic defect and nano to micrometer scale boundaries exist and scatter charge and heat carriers. TEM serves as a unique tool to reveal structural and compositional information, which can be employed to model the transport properties of thermoelectric materials. In this chapter, I focus on Mg₃Sb₂, an attractive candidate for thermoelectric devices due to its intrinsically low thermal conductivity and earthabundant elements. The p-type Mg₃Sb₂ suffered from poor performance and did not seem necessarily promising early in its development. (1-5) Although n-type Mg₃Sb₂ was first realized in the late 1950's it wasn't until recently it had first been studied and reported for its high performing thermoelectric properties. (6-8) With a peak ZT about double that of the p-type counterpart, the ntype Mg₃Sb₂-based materials would become the focus of much research in efforts to increase the performance by optimizing alloying, doping, and processing parameters.(9-17) The compound tends to have stability issues at elevated temperatures so some of the more attractive applications are for low-temperature waste-heat recovery TEGs and Peltier cooling devices. (18, 19) However, the PF suffered at low temperatures because of a thermally activated conductivity, in which the mobility of the charge carriers would be low at room temperature ($\sim 30 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and increase with temperature until about 550 K. At that point the mobility would decrease as the temperature



Fig. 4.1 Samples of Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01} showing the thermally activated conductivity and mobility with subsequent samples showing the improvement.(*20*)

continued to increase.(20–23) Increasing the mobility at low temperatures to improve the *PF* throughout the temperature range became one of the most significant and important improvements to the material's performance. Shuai *et al.* improved the mobility of Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01} by co-doping the compound with Nb.(22) Mao *et al.* made a similar improvement strictly through modifying process conditions, specifically by increasing the hot-press temperature.(20) Both enhancements of the carrier mobility were attributed to tuning the scattering mechanism from ionized impurity scattering (IIS), which is typically dominant at lower temperatures, to a mixed scattering of IIS and acoustic phonon scattering (APS).Fig. 4.1 shows the temperature dependent conductivity and corresponding mobility from Mao's *et al.* work.(20)

4.1.1 Motivation for This Study

Other TE materials besides Mg₃Sb₂-based compounds share this thermally activated mobility, which makes the phenomenon significant and relevant for study.(24–30) Despite the attention it has received, the exact mechanism behind this has remained an open question. For semiconductors of these carrier concentrations (10^{19} cm⁻³) this temperature dependent conductivity is quite irregular, as APS is expected to dominate the carrier transport and produce a negative temperature dependence.(*30*) It is certain that some scattering mechanism is responsible for the temperature dependent mobility, as carrier concentrations remain nearly constant through the temperature range.(20–23) One explanation, as mentioned above, involves Mg vacancies which can exist in significant amounts due to their low formation energy. The vacancies become charged point defect scattering centers, effectively acting as IIS.(20–23, 31–33) Considering the mobility due to IIS, we have(34)

$$\mu_i \propto \frac{\varepsilon_r^2 T^{3/2}}{N_i m^{*1/2}},$$
(4.1)

where ε_r is the dielectric constant and N_i is the impurity concentration. The mobility due to APS has the relation

$$\mu_l \propto \frac{1}{m^{*5/2} T^{3/2}},\tag{4.2}$$

and the total mobility is described by Matthiessen's rule by

$$\mu = \left[\frac{1}{\mu_i} + \frac{1}{\mu_l}\right]^{-1}.$$
(4.3)

The actual theoretical calculations for the mobilities are a bit more complicated even for a simple single-crystal, and would be much more so for a complex system such as the TE materials
discussed in this work. However, the trend in the temperature dependencies are accurate and could qualitatively explain the behavior of the carrier mobility as increasing with temperature initially, then decreasing as APS dominates at higher temperatures.

Contrary to the idea that IIS is responsible for the thermally activated mobility is the concept of grain boundary (GB) effects.(35-40) This is typically understood by a potential barrier due to an accumulation of charge carriers in the GB region. The electronic structure at the edge of the grain is different than that of the core due to defects, incomplete bonding, impurities, and lattice mismatch. Electrons from the grain core can transfer to trap states at the GB as the Fermi level equalizes across the region, ultimately forming a potential barrier that will scatter charge carriers and lower the mobility. The physics and chemistry at GBs can be quite complicated, and still little is known. Kuo et al. developed a two-phase model, treating the GB as a separate phase from the grain to describe temperature dependent conductivity that others have adopted and fit to their data.(39) Although there were some correlations between the model and measured values, some of the chosen parameters the predictions of the potential barriers are not entirely satisfying, and suppression of the scattering mechanism are primarily attributed to the grain size.(30, 41) Slade et al. has done interesting work regarding the calculated dielectric constant of certain TE materials. It was found with good correlation that materials with low dielectric constants were the ones that exhibited thermally activated mobility. They attributed this to the high polarizability in other materials allowing the GB potentials to be screened so less scattering would occur. However, this screening effect would also mitigate IIS if that were indeed the mechanism, so that shouldn't be considered conclusive evidence in favor of GB potentials as being the cause.

The fact remains that it can be very difficult to discern between the effects of IIS and GB potentials through analysis of the typical electronic properties. The intention of this study was to

add to the knowledge base regarding the debate over the proper microscopic description of the low-temperature scattering mechanism found in this important TE material. Despite all the attention on this topic there has been very little TEM study done to directly compare materials with and without the thermally activated mobility. Typically a direct microscopic comparison of two such separate materials would be like comparing apples and oranges, whereby drawing conclusions would be difficult. However, the work done by Mao *et al.* affords the opportunity to study two materials with the exact same stoichiometry in attempt to find clues about how the process conditions alone suppressed the scattering mechanism. The purpose of the TEM work here is to provide side by side microstructural comparison of Mg₃Sb₂-based materials in hopes of correlating defects with the low-temperature conductivity in order to gain insight to the true microscopic description of the thermally activated phenomena.

4.2 Experimental Methods

4.2.1 Materials Synthesis

Samples were synthesized, courtesy of Dr. Shaowei Song, to reproduce the mentioned work of Mao *et al.* The component elements of magnesium (Mg, 99.98%; Alpha Aesar), bismuth (Bi, 99.99%; Alpha Aesar), antimony (Sb, 99.8%; Alpha Aesar) and tellurium (Te, 99.999%; Alpha Aesar) were proportionally weighed according to the composition Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01}. The raw materials were loaded and sealed into a stainless steel jar with stainless steel balls in a glovebox under an argon atmosphere. After 10 h of ball milling the jar was returned to the glovebox where the powders were loaded into a 12.7 mm inner diameter graphite die. The loaded die was promptly hot-pressed after removing from the glovebox to minimize exposure to oxygen. Two

separate hot-pressings were performed under AC current at two different temperatures, 923 and 1073 K, with a pressure of ~80 MPa and a holding time of two minutes. One other sample was synthesized same as the above process but with the addition of niobium (Nb, 99.99%; Alfa Aesar) according to the composition Mg_{3.1}Nb_{0.1}Sb_{1.5}Bi_{0.5}Te_{0.01} and with the 923 K hot-press temperature.

4.2.2 Sample Preparation and Characterization

Bars with the dimensions of about 2 mm \times 2 mm \times 12 mm were cut from the disc shaped pressed samples to measure the temperature dependent resistivity and Seebeck coefficients. The measurements were taken in a Helium environment (Zem-3; ULVAC Riko) utilizing the fourterminal method to calculate the resistance. Two different sample preparations were used for TEM characterizations, bulk samples and powder samples. Bulk samples were polished by hand to about 30 µm thickness and finished with a 1 µm diamond paste. Either a dimple was made to further thin the sample or the edge of the sample was exposed, then subject to argon-ion beam milling (Gatan PIPS II) to sufficiently thin the sample for TEM. Ion beam energies and angles ranged from 2–3.5 keV and 2–4.5° respectively. Powder samples were made by pulverizing a small piece of the sample with a mortar and pestle in acetone for about 20 min. A drop of the solution containing micron-sized particles was placed onto a holey carbon grid. All TEM and EDS work was performed on a JEOL 2010F with a beam energy of 200 keV.

4.3 Results and Discussion

Fig 4.2 shows the temperature dependent conductivity measurements for the two Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} samples hot-pressed at 923 and 1073 K. The conductivity profiles were successfully reproduced as the sample hot-pressed at 923 K clearly exhibits a conductivity that is low at room temperature and increases with temperature until about 500 K. At that point the conductivity begins to behave as the 1073 K hot-pressed sample where APS dominates the mobility.

As mentioned Mg vacancies are thought to play a large role in the electronic properties of Mg₃Sb₂ based compounds, so the debate over GB effects vs. IIS as the source of the thermally activated conductivity could be just be a matter of where the Mg vacancies are located. If they were distributed throughout the grain they would most likely act as charged-point defects and



Fig. 4.2 Temperature dependent conductivity of the 923 and 1073 K hot-pressed Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} samples. The 923 K sample clearly exhibiting the thermally activated conductivity

cause IIS. However, if the Mg vacancies were largely concentrated at the GBs then the formation of potential barriers could be the proper description of the poor low-temperature carrier mobility. Kuo *et al.* used atom-probe tomography to study Mg₃Sb₂ based samples and found evidence of slight Mg deficiencies at a GB.(*40*) Although the resolution of atom-probe tomography is beyond the detection limits of the EDS used here, the thought that there may be a work around to this made the elemental composition at the GBs a reasonable place to start the investigation.

4.3.1 TEM Analysis of 923 K Hot-Pressed Sample

Fig 4.3a is a bright field TEM micrograph showing grains from a bulk sample preparation of Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} Unfortunately The thin areas of the sample preparation weren't wide enough to show a large network of grains, nor was is sufficient for HRTEM images. However The HAADF image in STEM mode (Fig 4.3b) was able to show the grains a bit more clearly and was adequate for EDS. Fig 4.3c is a line scan with the corresponding compositional profile. Knowing that the EDS would have difficulty detecting a compositional difference across a small distance measuring perpendicularly across a GB, the line was chosen to start in the middle of a grain and measure along the GB of two adjacent grains. The EDS did detect a measureable decrease in Mg, as well as an increase in Bi. This agrees well with the contrast in the HAADF image, as Bi with a higher atomic number will scatter the beam more than the other elements in the sample. This would suggest that there is a significant amount of Bi at the GBs. This was a promising result as it showed that it was possible and within the capabilities of the EDS to detect compositional variations at GBs. Another sample preparation was needed so more measurements were could be taken with hopes of obtaining larger thin areas in order to study more extensive grain networks. A bulk sample



Fig. 4.3 (a) Bright field TEM micrograph of Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} bulk sample showing grains. (b) STEM HAADF image showing more grains with slightly better visibility. (c) EDS line scan along a GB with corresponding compositional profile.

was prepared where the edge of the sample was thinned and exposed as opposed to a dimple as in the previous experiment, and the ion-beam milling was used with less aggressive parameters, as in lower angles and energies, and shorter time. Fig 4.4a is a bright field image of a few grains from the sample. Although a wide area of grains was not able to be viewed, there were improvements from the previous sample preparation. The GBs appear to be lined with dark spots, but the sample was still slightly too thick to obtain good HRTEM micrographs at the GB. Fig 4.4b is diffraction from the area. Although it was not a good pattern due to the thickness, there was enough symmetry to identify the Bi (012) and Mg₃Sb₂ (102) planes. Fig 4.4c is a bright field image at a location closer to the edge which is a thinner area, but was also subject to more ion-beam damage. Although the grain structure is not robust, there still appears to be a portion of a grain, where again the GB is lined with the black dots. Fig 4.4d is a HRTEM micrograph at the sample edge where it was thin enough to observe lattice structure. The lattice spacing on the very outer edge was measured and matched the Bi (012) plane. A lattice structure separated from a clear boundary was identified by the measured spacing to be the Mg_3Sb_2 (102) plane. These are some important differences from the previous sample, as there appears to be plenty of crystalline Bi segregated from the core material. STEM was performed to further study the black dots that seem to define the GB. HAADF imaging is much more adept to thicker samples, so the ability to observe wider areas was expected and seen in Fig. 4.5a. The HAADF image shows the grain boundaries clearly defined by white dots which seem plentiful throughout the sample. Fig 4.5b is an EDS line scan through the boundary indicated by the arrow. As opposed to the previous sample preparation, the Bi found here is clearly segregated as indicated by the sharp peaks from the Bi signal. Fig 4.5c is an EDS



Fig. 4.4 (a) Bright field image of. Mg3.2Sb1.5Bi0.5Te0.01 sample prepared from less aggressive ion-beam milling. (b) Diffraction where Bi (012) and Mg3Sb2 (102) planes are identified. (c) Bright field image near sample edge showing some GB structure. (d) HRTEM near sample edge where Bi (012) and Mg3Sb2 (102) planes are identified.



Fig. 4.5 STEM of Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} from less aggressively ion-beam milled sample (a) HAADF showing grains defined by precipitated Bi. (b) EDS line scan through a boundary in (a) indicated by the arrow identifying the Bi. (c) EDS elemental map overlaid onto area with large Bi segregations. (d) HAADF showing a wide area of grains all with Bi precipitates defining the GBs

elemental map overlaid onto the HAADF image showing how large some of the Bi segregations were. This was very common throughout the sample, which is further illustrated in another HAADF that shows a fairly wide area of grains defined by Bi-lined GBs (Fig 4.5d).

The two experiments above are good examples of the importance of TEM sample preparation and illustrate how it can affect what is observed. A good understanding of this is crucial toward proper analysis, and the particular questions that need to be answered should always be considered when determining how to prepare a sample. The true initial state of the material will never be observed in TEM, as artifacts from sample preparation will always be present in a specimen. Since the appearance of Bi varied with the sample preparation parameters, the question arising at that point was whether or not the segregated Bi was an artifact of the sample preparations herein, particularly from the ion-beam milling and the mechanical polishing. A third sample preparation was employed to help answer this question, being a powder preparation that didn't involve any polishing or ion-beam milling. Fig. 4.6a is a low magnification bright field image of a particle from the powder sample showing plenty of mass-thickness contrast. STEM was performed where Fig. 4.6b is an EDS elemental map overlaid onto a HAADF image. The concentrations of Bi, in blue, are quite clear and seemingly in greater amounts than the bulk sample preparation. Further verification of the Bi is in the line scan taken from the middle of the large central particle. The segregations here are large, up to a few hundred nm. Fig 4.6d is a higher magnification HAADF image of a smaller particle showing with good definition how well the Bi segregations are distributed across the surface of the particle. A line scan was taken through the center of that particle as well, and is found in Fig. 4.6e



Fig 4.6 (a) Low magnification bright field micrograph of the Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} powder sample showing significant mass-thickness contrast. (b) STEM-EDS elemental map overlaid onto HAADF image displaying large and plentiful Bi segregations. (c) EDS line scan from (b) showing tightly packed Bi crystals. (d) Higher magnification HAADF showing the embedded Bi with good definition. (e) EDS line scan from (d) further confirming the Bi presence.

From the powder sample results the Bi segregations appear to be a product of the synthesis and not an artifact of sample preparation. It was both unexpected and interesting to find so much Bi excluded from the host matrix, as to my knowledge segregations to such an extent has not been previously reported. Small precipitates and accumulations have been found in other studies of Mg₃Sb₂-based compounds, but not to this extent or in a situation such as this.(*42–45*). The natural question arises of how much does the extensive Bi segregation have to do with the low temperature conductivity, and whether or not the sample hot-pressed at 1073 K shares this condition.

4.3.2 TEM Analysis of 1073 K Hot-Pressed Sample

Considering the results from the three sample preparations for the 923 K hot-pressed sample, the powder preparation was most effective at exposing the Bi for TEM measurements, as the ion-beam milling appeared to destroy it. Fig 4.7a is a HAADF image of a particle that showed some areas of contrast that were investigated. EDS line scans were performed on several areas of contrast where two selected scans are shown, 4.7b being on outer edge of the particle, and 4.7c at the center. The Bi signal is nowhere near the relative strength as the 923 K sample, as it remains less than the Mg signal. Moreover, any increase in the Bi signal is accompanied by a similar contour in the Mg signal. This is an indication that the areas of contrast are due to variations in thickness of a fairly uniform composition, and not segregated Bi as in the previous sample. Several areas were examined on this particle as well as on other observed particles, and this particle was very typical of the entire sample, all with similar results and no evidence of Bi segregation.



Fig. 4.7 (a) HAADF image of a typical particle from the powder preparation of the 1073 K hot-pressed sample. (b) EDS line scan from an area of contrast on the outer edge of the particle. (c) Line scan from an area of contrast at the center of the particle.

The results strongly suggest that the lower hot-press temperature is the reason behind the segregated crystalline Bi in the 923 K sample, and is obviously well correlated with the poor conductivity. Seeing the Bi phase to this extent in the 923 K sample may be unexpected, but the association between the presence of Bi and the poor conductivity in Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} is not unheard of. Shang *et al.* found Bi phase through both X-ray diffraction and EDS via scanning electron microscopy.(*45*) However there were some important differences between this experiment and hers. The samples in that study were hot-pressed at 1073 K where no Bi phase was found initially, which is consistent with the results here. The appearance of Bi came only after thermal

stability tests, most notably at a temperature of 773 K. Considering both results it seems the ability of Bi to be well incorporated into the matrix tends to be sensitive to temperature, whether it be during synthesis or during its intended operation. This issue has also been observed in other Zinlt materials, as Shuai *et al* found Bi phase in CaMg₂Bi₂ through X-ray diffraction and differential scanning calorimetry.(*46*) In that work the thermoelectric properties were not optimized until the Bi phase was eliminated by reducing the stoichiometric amount in the composition.

To gain insights on how this segregation affects the low-temperature conductivity, consideration should be made to the effects Bi alloying has on the electronic properties of the system when properly incorporated into the matrix. The proper way to view the effects of Bi alloying is to compare the evolution of properties between Mg₃Sb₂ and Mg₃Bi₂. The closely matched lattice constants can be owed to the small difference in atomic radii between Sb and Bi, and is a key factor in the enhancements of the TE properties.(47, 48) Isoelectronic alloying typically has the intention to utilize mass differences in order to suppress κ_l primarily through mass fluctuations in the lattice.(49-51) For the compound Mg₃Sb_{2-x}Bi_x we should also expect the electronic properties to shift from Mg₃Sb₂ to Mg₃Bi₂ as x increases. It has been shown both experimentally and from calculations that the effective mass decreases as x increases, which in turn benefits the mobility.(52-54) The energy band structures of Mg₃Sb₂ and Mg₃Bi₂ illustrate some important differences between the two compounds, and can be seen in Fig. 4.8.(48) The effective mass is inversely proportional to the conduction band concavity, where we see the concavity on the conduction band minimum is much higher in Mg₃Bi₂ than in Mg₃Sb₂(34) The discrepancy in the bandgaps (E_g) can also be seen, where E_g for Mg₃Sb₂ is indirect and accepted



Fig. 4.8 Energy band structure of Mg_3Sb_2 and Mg_3Bi_2 showing the differences between the two.(48)

to be ~ 0.7 eV. Mg₃Bi₂ is actually considered a semimetal where its E_g is nearly direct and close to 0 eV. Adjusting the amount of Bi in the compound amounts to an opportunity for tuning the band structure to provide a lower effective mass and making the optimal carrier concentration easier to achieve.(48) The more Bi segregated from the matrix would mean a loss of these advantages and could result in poor low-temperature conductivity.

The Bi crystals could present another issue regarding electron mobility by acting as scattering centers themselves. Although Bi has an electrical conductivity over an order of magnitude higher than the values shown in Fig. 4.2, the difference in work function between the two phases could create a potential barrier and depletion region at the interface. Semimetal-semiconductor interfaces are known are known to create Schottky-like barriers with semimetal thicknesses on the order of the particle sizes observed here.(55–57) In fact nm-sized layers of Bi



Fig. 4.9 Schematic of the energy band diagram of a Schottky junction showing that a potential barrier at the interface is the difference between the work function of the metal and the electron affinity of the semiconductor.(62)

and other semimetal-semiconductor interfaces exhibit significant rectifying behavior, and have been studied and developed for applications.(58–61) A simplified schematic of such a potential barrier, ϕ_B is illustrated in Fig. 4.9(62) and is calculated by the equation

$$e\phi_B = e(\phi_m - \chi), \tag{4.4}$$

where *e* is the fundamental charge, ϕ_m is the work function of the metal, and χ is the electron affinity of the semiconductor.(*34*) For Bi we have $\phi_m \approx 4.2$ V, and for Mg₃Sb₂ we have $\chi < 3.8$ V.(*63*) Thus there would be an energy barrier of at least 0.4 eV. This effect is not restricted to the interface, as a depletion region will extend into the semiconductor, with a width given by

$$W_D = \sqrt{\frac{2\varepsilon_s}{eN_D}} \left(\phi_B - \frac{k_B T}{q}\right),\tag{4.5}$$

where ε_s is the permittivity of the semiconductor ($\varepsilon_r \cdot \varepsilon_0$), and N_D is the donor dopant concentration.(34) Taking N_D as the measured carrier concentration from literature as $\approx 3.7 \times 10^{25}$

m⁻³, and $\varepsilon_r = 32$ we can calculate $W_D \approx 6$ nm.(22, 30) This may be small compared to fabricated Schottky devices, but could be a significant distance when considering the scale of the Bi crystallite distribution in Fig. 4.6d. This potential barrier and depletion region could serve as temperature dependent scattering centers and contribute to the poor mobility at low temperatures. Bi also has a relatively low melting point at 544 K, which is very close to where the conductivity profiles of the 923 and 1073 K samples converge. Shuai found that the Bi signal from the X-ray diffraction vanished above the melting point, but returned once the sample cooled again. In this situation the Schottky barrier would vanish past the melting point, and return once the sample cooled. If the Bi segregations are concentrated at the GBs, as it appears so in Fig. 4.5, this could be why Mg₃Sb₂ seems to exhibit GB dominated charge carrier transport, as other studies have shown potentials due to precipitate accumulation at GBs.(*64*)

4.3.3 TEM Analysis of Niobium-Doped Sample

The interesting case of the Nb-doped sample (Mg_{3.1}Nb_{0.1}Sb_{1.5}Bi_{0.5}Te_{0.01}) is the third sample tested here, where Fig. 4.10 shows the significant improvement in the low temperature conductivity even when the sample is hot-pressed at 923 K. Fig. 4.11a is a HAADF image of a typical particle from a Nb-doped powder sample. The appearance of well-defined high-contrast areas closely resembles the 923 K hot-pressed sample. The EDS elemental maps in Fig 4.11b show that the light areas from the HAADF image are indeed Bi segregations. Fig 4.11c further confirms this as the line scan shows a well-defined Bi signal. This indeed is a curious result as the addition of the Nb seems to suppress the low temperature scattering mechanism regardless of the presence of the Bi. Mao worked with samples similar to Mg_{3.1}Nb_{0.1}Sb_{1.5}Bi_{0.5}Te_{0.01} but using transition



Fig. 4.10 Temperature dependent conductivity of the 923 K and the Nb-doped sample also hot-pressed at 923 K.

metals other than Nb while obtaining very similar results, particularly with Co as the codopant.(65) Powder neutron diffraction results in his work show that the Mg vacancies can be partially filled by the Co, as a result controlling the defects to some degree. It has also been presumed that Nb doping could increase ε_r , as trace amounts of dopants are known to significantly affect ε_r in some cases.(22, 66–69) This in turn would increase screening effects and help suppress IIS. When comparing the Nb-doped sample to the 1073 K hot-pressed sample, it could be possible that each modification enhances the low-temperature mobility by different means. Whereas the elimination of the segregated Bi by the high-temperature hot pressing, and the Nb's doping effect, may be suppressing two separate scattering mechanisms



Fig. 4.11 (a) STEM HAADF of Mg_{3.1}Nb_{0.1}Sb_{1.5}Bi_{0.5}Te_{0.01}. (b) EDS elemental maps showing non-uniform distribution of Bi. (c) Line scan showing well-defined Bi signal coinciding with the contrast.

4.4 Conclusion

This work has presented a TEM microstructural study of Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01}, in particular regarding the issue of low temperature thermally-activated conductivity. Different sample preparations were used to discern between artifacts of sample preparation and features of interest within the specimen. It was seen that the appearance of segregated crystalline Bi, a feature of particular interest, tended to be sensitive to ion-beam milling and was nearly eliminated when the milling was over used. It was found that a powder sample preparation, although not a traditionally

desirable preparation for bulk samples, was particularly helpful in observing the extent of the Bi segregation in the 923 K hot-pressed sample. In fact an important lesson was learned, as much effort was applied to the bulk sample preparation in order to replicate results from literature, when all the while the most interesting feature within the sample was being destroyed. The presence of the Bi phase in Mg₃Sb₂-based compounds was found to be associated with poor conductivity and TE performance in other studies, and correlated with the thermally activated conductivity in this work. A mechanism was proposed as a possible means by which the Bi crystallites may act as scattering centers due to the difference in work functions forming a potential barrier and a depletion region. Despite the presence of Bi, the Nb-doped sample showed a similar improvement to the low temperature conductivity. It is possible that the Nb-doping and the high temperature hot-pressing suppress two separate scattering mechanisms. Considering the complexity of such a system, I believe that cause of this behavior at low/room temperatures is not just the action of one simple mechanism, but more likely to be a combination of mechanisms working together to produce this property. However, whether the segregated Bi is the source of the thermally activated conductivity, or just a symptom of the same problem will require more study.

4.5 Bibliography

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Chapter V Summary and Perspective

5.1 Summary

As presented in this dissertation, my TEM studies have provided valuable information to explain the performance of water electrocatalysts and Mg₃Sb₂-based thermoelectric materials. This chapter is a summary of the understandings and outlook of future work in this area.

5.1.1 Water-Splitting Catalysts

Hydrogen-producing electrolysis technologies have been trying to increase its footprint into the energy infrastructure for several years. Despite efforts toward integrating hydrogen fuel as a primary energy carrier, the cost per kWh of hydrogen systems remain well away from the demanded targets. Although there are several financial and economic obstacles, one of the largest is the cost by which hydrogen can be produced. One of the keys to overcoming this barrier is the development highly efficient and low-cost electrocatalyst that operate directly in seawater. The overpotentials associated with sluggish reaction kinetics are the largest burden on efficiency, and a catalyst's composition and structure has a huge influence on the kinetics. The synergistic combinations of different species as well as crystalline and amorphous structures are considered to be critical elements toward enhancing a catalyst's performance. This makes confirmation of such features a critical step in advancing the development of these systems, and the TEM analyses of the works presented in this dissertation were able to do just that. The work on the sulphur-doped nickel/iron (oxy)hydroxide showed that an extremely facile, scalable, and energy-efficient synthesis technique was able to form the porous and amorphous structures necessary for good OER performance. Before and after TEM analyses of the B-Co₂Fe LDH catalyst was used to show how a clever boron modification was able to improve the LDH system, which is an important structure within the field. A similar analysis approach was employed in the CoP_x@FeOOH experiment, as the analyses were able to successfully verify the formation of the FeOOH shell about the CoP_x nanowire core. The core-shell structure exhibited excellent OER performance in seawater while providing protection to the system in the corrosive environment.

5.1.2 Mg₃Sb₂–Based Compounds

Thermoelectrics are another important green-energy technology trying to gain traction in commercial and industrial settings. The advantages for TEGs are well known, being solid-state devices requiring little to no maintenance with the ability to convert otherwise wasted heat energy into useable electricity. This ability to improve the overall efficiency of high energy-consuming plant installations, vehicles, residential applications, etc., could make a meaningful impact on the world's energy consumption. This technology could almost be immediately applied, as it would require no major infrastructure changes and could adapt to existing systems with relative ease. Unfortunately the low power conversion efficiency of current TEGs restrict their use to niche applications, and the TE materials need significant improvements to make a real impact on markets and industry. The use of earth–abundant materials is important to the success of the technology, and this is why Mg₃Sb₂-based compounds are some of the most important developments in the field However, they tend to suffer from degradation at high temperatures and can exhibit poor conductivity at lower/room temperatures. The phenomena of the thermally activated conductivity

was studied via TEM where a direct comparison were made of two Mg_{3.2}Sb_{1.5}Bi_{0.5}Te_{0.01} samples that both did and did not exhibit the property. The two materials had identical stoichiometry, but different process conditions. Although the low temperature conductivity had been improved, the underlying mechanism is still an open question in which the answer could greatly benefit materials engineering efforts in regard for this system as well as others. This study found segregated Bi crystals in 923 K hot-pressed sample that were not present in the higher conductive 1073 K sample. The correlation between the presence of the Bi and the poor conductivity was an interesting discovery, where a mechanism was proposed to where the Bi crystals could act as temperature dependent scattering centers. More work should be done to determine if segregated Bi plays a role in the thermally activated conductivity, or if it is just a byproduct of a different problem. The case of the Nb-doped 923 K hot-pressed sample was curious, as is showed an improvement in the conductivity while Bi segregations were still present. This system may be helpful towards studying the effects the Bi has on conductivity. It is possible the higher hot-pressing temperature and the Nb-doping address two different scattering mechanisms. In other words it seems that typical IIS due to Mg vacancies is not the only mechanism, but likely a combination of things contributing to the overall effect.

5.2 Perspective

TEM can be used to observe electronic properties as well as microstructure, especially with *in-situ* TEM techniques, where microstructure and external stimulations (electrical, mechanical, thermal, etc.) can be simultaneously observed. A concept mentioned earlier that was not addressed in this work was idea of the thermally activated conductivity being a result potential barriers at

grain boundaries. It is thought by many that a variety of defects found at GBs can contain unoccupied energy states not found in the bulk. Charge carriers can diffuse into the GB as the Fermi levels of the GB and bulk phases equalize. The accumulation of charge creates a scattering potential and an energy barrier that must be breached for the charge carrier to propagate. The conductivity due to the thermionic emission across the, GB (σ_{GB}), can be modeled as follows:(1, 2)

$$\sigma_{GB} = e^2 Ln \left(\frac{1}{2\pi m^* k_B T}\right)^{1/2} exp\left(\frac{-E_b}{k_B T}\right),\tag{5.1}$$

where *L* is the grain size, *n* is the charge carrier density, and E_b is the energy barrier. Kuo *et al.* developed a two-phase model with the intention to capture the overall conductivity within the grain (σ_G) and across the GB through the equation(3)

$$\sigma^{-1} = (1-t)\sigma_G^{-1} + t\sigma_{GB}^{-1}, \qquad (5.2)$$

where *t* is the length fraction of the GB phase. However, if we are only concerned with the portion of the conductivity profile associated with the thermal activation, we can assume $\sigma_{GB} \ll \sigma_G$ and make the approximation $\sigma \approx \sigma_{GB}$. Making this substitution into Eqn. 5.1, then taking the natural log of both sides we get

$$\ln \sigma = \frac{-E_b}{k_B T} + C , \qquad (5.3)$$

in which plotting $\ln \sigma$ vs. $1/k_BT$ should give us a slope of $-E_b$ on the thermally acticated portion of the conductivity data. This treatment of the 923 K hot-pressed sample is seen in Fig. 5.1. From the fitted data a value is extracted of $E_B = 55$ meV, which is quite agreeable to calculations in literature.(2–4) Despite the ability to fit models and make calculations, these potentials will need a measurement in order to verify whether or not they exist as predicted.



Fig. 5.1 Conductivity data from 923 K hot-pressed sample fitted according to Eqn 5.3

5.2.1 Kelvin Probe Microscopy

The Kelvin probe, first conceptualized and performed by Lord Kelvin, has the ability to measure surface potentials and has been used in conjunction with atomic force microscopy (AFM) since 1991, as first done by Nonnenmacher *et al.*(5) Kelvin probe microscopy (KPM) can detect potentials on semiconductors, as well as other materials, with nanometer lateral and millivolt electric potential resolutions.(6) The principal of KPM relies on the difference in work functions between a location on the sample and the tip of an AFM probe, which is shown schematically in Fig. 5.2.(6) A sample and tip with different work functions, ϕ_s and ϕ_t , (Fig 5.2a) are brought in



Fig. 5.2 (a) An AFM tip and sample with two different work functions. (b) Tip and sample in close proximity and electrically connected facilitating charge flow and a contact potential difference. (c) A DC bias applied equaling the contact potential difference to cancel the effect.(6)

close proximity while electrically connected so charge carriers can flow between them to equalize the Fermi levels and create a contact potential difference (V_{CPD}) between the two (Fig 5.2b). The charge separation induces an electric field which will in turn cause a deflection in the cantilever of the AFM probe. When a DC bias equal but negative of the V_{CPD} is applied to the tip and sample the potential difference between the two will be canceled, and thus the V_{CPD} can be known. The deflection alone is not suitable for detection, so an AC voltage at the resonant frequency of the cantilever is superimposed onto the DC bias. We can see the role the AC signal plays as the electrostatic force is modeled by the capacitance between the tip and sample:

$$F_E(z,t) = -\frac{1}{2} \frac{\partial C(z)}{\partial z} \left[(V_{DC} \pm V_{CPD}) + V_{AC} \sin(\omega t) \right]^2, \qquad (5.4)$$

where C(z) is the capacitance as a function of the distance z from the sample to the tip, ω is the driving frequency, and V_{DC} and V_{AC} are the DC bias and the AC amplitude respectively. Expanding the voltage term we get

$$F_E \propto \left[(V_{DC} \pm V_{CPD})^2 + 2(V_{DC} \pm V_{CPD}) V_{AC} \sin(\omega t) + \frac{V_{AC}^2 (1 - \cos(2\omega t))}{2} \right].$$
(5.5)

When V_{DC} cancels out V_{CPD} the first two terms vanish, and since the third term is out of phase with the driving signal and not of the first resonant mode of the cantilever, the tip will have little to no vibration. As mentioned above, $V_{CPD} = \phi_t - \phi_s$, where a precise value of ϕ_t is needed to know ϕ_s . However, when measuring the potential between two spots, 1 and 2, on a sample we have,

$$\Delta V_{CPD} = (\phi_t - \phi_{s1}) - (\phi_t - \phi_{s2}) = \phi_{s2} - \phi_{s1}$$
(5.6)

where the work function of the tip is conveniently not needed.

5.2.2 KPM in-situ TEM

KPM in has seen some success in mapping potentials across grain boundaries, but with AFM the potential maps are only accompanied with the topographical information from a previous measurement.(4, 7) KPM used as an *in-situ* TEM technique (TEM-KPM) could have benefits not seen before with these types of electrostatic measurements. This *in-situ* technique has the advantage of combining the structure and composition data and to take pinpoint potential measurements across GBs and other defects precisely identified by the TEM. TEM-KPM could be realized by the use of Humming Scientific's Nano-Manipulation holder, and this is illustrated in Fig. 5.3. A modified AFM tip can be fixed to a biasing enabled probe which can access features



Fig. 5.3 Illustration of Humming Scientific's Nano-Manipulation holder.

on samples with nanometer precision. Vibration of the tip will be able to be viewed, and when the correct DC bias is applied the user will be able to observe the vibration stop.

5.2.3 TEM-KPM Experimental Setup

Work has been done on an experimental setup for TEM-KPM, where a compatible configuration of necessary electronics have been compiled. Fig 5.4a is a simple schematic of the setup and Fig 5.4b is a picture of the setup in the TEM room. A signal generator isolated from



Fig. 5.4 (a) Schematic TEM-KPM setup with adding circuit diagram. (b) Picture of TEM-KPM setup in the TEM room.
earth ground is necessary as to not interfere with the TEM's internal grounding. This was done with an MHS-5200A direct digital synthesis function generator powered by a simple benchtop DC power source, as opposed to using the supplied wall transformer supplied with the unit. The high precision DC source for biasing was provided by a Keithley 2400 source meter, where the DC bias was mixed with the AC signal with a simple adding circuit seen in Fig. 5.4a. A pc-based oscilloscope (Hantek 6022BL) was used to monitor the signal output to the holder, where the signal mean was used as an accurate measure of the applied DC bias output from the adding circuit.

TEM-KPM probes were made from modified AFM probes that had the base trimmed to about 1mm in width with a pen-sized diamond etching tool to accommodate the allowable space. The modified probe was fixed to a section of gold wire with conductive epoxy for insertion into the Nano-Manipulation holder. Figs. 5.5a,b are optical microscope images of the constructed probes. The matter of samples for use and their preparation was addressed by preparing test specimens that could have predictable measurements in order to calibrate the system. In the case of simply measuring the work function of a metal, gold would be used as its properties are well known and would make for a straight forward comparison. For the purposes of measuring a variation of potential along a surface we would need a test specimen that was sure to exhibit a significant potential difference across an interface. For this a commercially available Schottky rectifier was used, namely a STPS20120D model supplied by Mouser. The device consists of an n-type silicon semiconductor with a titanium-tungsten alloy for the metal layer which produces a built-in potential of about 0.6 V with no forward bias at room temperature.(8) Fig 5.5c is an image of a prepared specimen from the device epoxied to copper foil suitable for the holder. The device specimen was sanded and polished to remove the external coating to expose a cross section of the



Fig. 5.5 (a) Modified AFM probe shown epoxied to gold wire. (b) Higher magnification of (a) showing the cantilever and AFM tip. (c) Prepared TEM-KPM calibration specimen from STPS20120D Schottky rectifying device cross section. (d) AFM tip approaching the surface of gold specimen.

device layers. From the bottom of the image up is the large copper backing layer of the device with a metal layer above it for ohmic contact to the semiconductor. Above that layer is the n-type silicon with the thin titanium –tungsten alloy layer for the Schottky interface. The top left corner of the sample has the remainder of the contact metal for the device leads. The specimen was polished into a wedge shape so that the exposed layer side came to a sharp edge to be more suitable for TEM observation.

5.2.4 Experimental Results

The hardware was configured as mentioned above with the AC driving frequency set to 250 kHz according to the resonant frequency of the Nano Sensors SPL series-021 AFM probe used. Fig. 5.5d shows the tip approaching the gold specimen with a separation distance on the order of 10 nm. The AC amplitude was initiated at 0.1 V and slowly ramped up to 3.0 V, being suitable ranges for typical KPM measurements.(9) No action on the cantilever was detected despite the oscilloscope confirming that the signal was applied to the holder. Systematic adjustments were made to attempt to observe the phenomena, particularly regarding alignment and driving frequency. First the alignment of the tip and sample was carefully adjusted while the signal was kept constant. The position on the z-axis (in and out of the page) of the tip can be compared to the sample's position in two ways, observing the focus of the objects and by the wobbler. When either the focus or the wobbler differ significantly between the sample and the tip it will be the case that the two are well out of alignment. Adjustments within this range were made while successively increasing the AC amplitude upon each attempt. Unfortunately no deflection or vibration was observed throughout the adjustments.

Another variable was considered, that of the driving frequency of the signal generator. The specification for the resonant frequency for the AMF probe is not precisely stated by the manufacturer but is rather given as a range, namely 200-300 kHz. The above adjustments were performed as iterations of increasing AC amplitude upon varying the tip-sample alignment. One more layer of iteration was incorporated, which was to perform the above adjustments throughout the given resonant frequency range in steps of 10 kHz. Despite the efforts the phenomena was not observed as no vibration of the cantilever was seen.

There are a few issues that can addressed in order to troubleshoot the experiment for continued work. One could be issues caused by the resistance created by the conductive epoxy between the gold wire and the base of the AFM probe. This resistance would not affect the signal, since the AC circuit is open with no current to create a voltage drop. However, it could be affecting the flow of electrons as the Fermi levels of the tip and sample equalize and create the potential difference. The use of a pico-ammeter may be able to detect this current flow and may help to see if the charge is transferring as shown in Fig 5.2b, that is if the signal to noise ratio would be high enough for such a measurement. Another issue regarding the charge transfer is the issue of the direct connection required to facilitate it. Several times during the mentioned experimental attempts, a connection was manually performed outside the holder with the tip in position in order to see if the phenomena could be observed. It did not seem to help as no deflection or vibration was not detected. It is unclear from my literature search of KPM if this is part of the process in a typical KPM setup.

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Appendix

List of Publications

- 1. L. Wu, L. Yu, B. McElhenny, X. Xing, D. Luo, F. Zhang, J. Bao, S. Chen, Z. Ren, Rational design of core-shell-structured CoP_x@FeOOH for efficient seawater electrolysis. *Appl. Catal. B Environ.* **294**, 120256 (2021).
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- A. J. Wang, E. P. Dillon, S. Maharjan, K.-S. Liao, B. P. McElhenny, T. Tong, S. Chen, J. Bao, S. A. Curran, Resolving Nanocomposite Interfaces via Simultaneous Submicrometer Optical-Photothermal Infrared-Raman Microspectroscopy. *Adv. Mater. Interfaces.* 8, 2001720 (2021).
- 4. L. Wu, L. Yu, F. Zhang, B. McElhenny, D. Luo, A. Karim, S. Chen, Z. Ren, Heterogeneous Bimetallic Phosphide Ni₂P-Fe₂P as an Efficient Bifunctional Catalyst for Water/Seawater Splitting. *Adv. Funct. Mater.* **31**, 2006484 (2021).
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