# Synthesis and Atomic-Scale Characterization of Oxide Thermoelectric Materials and Devices

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#### THESIS

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- My father, Abed Alhadi, "may God bless his soul" and my mother, Nazeh, they taught me to never give up, and to work hard to achieve my goals.
- To my wife, Rana, without her unlimited support and patience it would never have been accomplished.
- To my children, Noor, Yazan, Noreen and Lana.

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# LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
CCD	Charged Coupled Device
CVD	Chemical Vapor Deposition
EDS	Energy- Dispersive X – Ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
FIB	Focused Ion Beam Microscopy
PLD	Pulsed Laser Deposition
PVD	Physical Vapor Deposition
PPMS	Physical Properties Measurements
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
TEG	Thermoelectric Generator
TEM	Transmission Electron Microscopy
XPS	X- Ray Photoelectron Spectroscopy
ZT	Thermoelectric Figure of Merit

#### SUMMARY

Energy harvesting research has garnered increasing attention over the last decade. There are two ways to harvest energy, either by harvesting the primary energy from sources like the sun, wind, water, *etc.*, or by harvesting energy from secondary sources like wasted energy or mechanical vibrations. Approximately, 90 percent of the primary energy is first converted to heat with ~ 60-70 percent of this heat being lost as waste heat. The capability of harvesting even a small fraction of this waste heat would significantly enhance the efficiency of the power generating system, lower the pollution that these systems exhaust to the environment and enhance the global economy. Thermoelectric generators are potential candidates for power generation. Thermoelectric generators are solid-state devices that can convert heat to electricity. Seebeck discovered this phenomenon in the early eighteenth century. However, there have been little widespread applications due to the low efficiency of the devices. Recently, researchers have reported enhanced efficiencies for thermoelectric devices due to advances in nanoscience and nanofabrication techniques.

Sub-atomic levels in nanoscale materials are discrete which allows tuning of the properties of the materials and engineering of new materials. Our research focused on oxides as candidate thermoelectric materials, specifically niobium doped strontium titanate and vanadium niobium co-doped strontium titanate and iron doped strontium titanate. These materials have a comparable power factor to the state-of the-art, bismuth telluride, with the added advantage of nontoxicity and suitability for high temperature applications. The main challenge is the synthesis of new, doped oxide thermoelectrics and tailoring of the thermal conductivity, which is inherently low in this class of materials. Since most of the physical properties of the materials are a function of temperature, our research started first, with a TEM *in-situ/ex-situ* thin film annealing study.

## **SUMMARY** (continued)

Our objectives from this study were to understand the heat transport and its effect on the film morphology and the physical properties. Second, since nanostructures have demonstrated a capability of lowering the thermal conductivity, thin films of doped strontium titanate were synthesized by pulsed laser deposition. Scanning transmission electron microscopy, energy dispersive x-ray spectroscopy, x-ray photoelectron spectroscopy, and atomic force microscopy were used for atomic-scale characterization of the thin films. The electrical and transport properties of the thin films were measured by a physical property measurements system. Control of the defect chemistry and concentration is important for producing highly efficient oxide thermoelectrics. This study suggests that doped strontium titanate is a promising material for thermoelectric energy harvesting.

#### **CHAPTER 1**

# **INTRODUCTION**

# 1.1 Energy Harvesting

Energy by definition is the thermodynamic property of materials that can be converted from one form to another but it cannot be created or destroyed. We are surrounded by many energy sources, *i.e.*, natural sources like wind, solar, etc., and thermal energy like the heat from vehicles, power plants, computers, and the human body. Light energy similar to sunlight and mechanical energy like vibration and human motion may also be harvested. Harvesting these various energy forms requires different processes and device technologies. For example, photovoltaic devices are used to harvest light energy, micromechanical devices for generating energy from motion and mechanical vibration and thermoelectric devices for waste heat. The focus of this study is on complex oxides for the harvesting of waste heat.

The efficiency of most of the thermal systems, i.e., cars, power plants, etc., is less than 40 percent which means more than 60 percent of the primary energy is lost as waste heat. Moreover, if we increase the efficiency of these systems, it would have a big impact on the global economy. On the other hand, most of these systems use fossil fuels, with their output to the environment being carbon dioxide, carbon monoxide, etc., According to the Union of Concerned Scientists, 60 percent of U.S. transportation emissions come from cars and light trucks. These types of emissions are widely believed to pollute the environment, causing climate change resulting in severe global weather [1]. Since more than 90 percent of the primary global energy is first converted to heat, thermoelectric generators (TEG) have the potential to increase the efficiency of the use of our primary energy

enhancing the economy and lowering atmospheric pollution. TEGs are solid-state systems, i.e., no moving parts with the input being heat and the output is electricity. To illustrate, let us take the vehicle system Figure 1.1 as an example. Sixty to 70 percent of the energy that produced by chemical energy of the internal combustion engine is a lost through the exhaust and the cooling systems. Recovering just five percent of this energy utilizing a TEG could re-charge the battery free of maintenance by replacing the alternator, which consumes five percent of the input energy. This new configuration would result in ~10 percent recovery of the wasted energy. Furthermore, if we have a high efficient thermoelectric material, one could replace the cooling system by solid-state-cooling device which might lead to very efficient vehicles.



Figure 1.1 - TEG for replacing the alternator (free maintenance battery charger)

#### 1.2 Background

The operation of a TEG is governed by the Seebeck effect. In 1821 Seebeck discovered that a compass needle could be deflected by a closed loop formed by joining of two different materials in the presence of a temperature gradient [2]. Seebeck thought it was due to magnetism induced by the temperature difference [3]. He later realized that the phenomenon was due to a different force called the thermoelectric force. The proportionality constant between the voltage produced and the temperature gradient is called the Seebeck coefficient (S), which has units of ( $\mu$ V/K). In 1834 Peltier found that an electrical current would produce cooling or generate heat at the junction of dissimilar metals. The proportionality constant between the current I and the cooling or heating q is known as the Peltier coefficient (II) as described in the following equation:

$$\Pi = \frac{q}{I} \tag{1}$$

The relationship between the Seebeck and Peltier coefficients was later developed by Lord Kelvin [4]. As shown in Eq. (2).

$$\Pi = TS \tag{2}$$

The science of thermoelectricity and thermoelectric materials further developed from 1920 - 2000, however, there was very little commercial impact. Ioffe developed a modern theory of thermoelectricity using the concept of the thermoelectric figure of merit (ZT) [5]. As defined in Eq. (3)

$$ZT = \frac{S^2 \sigma}{k} T \tag{3}$$

There were some isolated applications like the radioisotope thermoelectric generator (RTG) for NASA space missions and some industrial applications for the Peltier cooling system, but the low efficiency of the systems inhibited the growth of the thermoelectrics industry. Thermoelectric materials (TE) have only recently received a lot of interest for conversion of heat to electricity. The recent attention is due to the possibility of enhancement of the efficiency of TE materials and devices at the nano-scale. Typical compound semiconductors like bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>) are used in TE devices. However, the need for materials that are stable at high temperatures and in the presence of high humidity has led to the search for new, more efficient materials.

Complex oxides are excellent candidates for use in high temperature thermoelectric devices. The key challenge is optimization of the TE figure of merit (ZT). Despite the high thermal conductivity present in most oxides, the power factor ( $S^2\sigma$ ) of materials like doped strontium titanate (SrTiO<sub>3</sub>) rivals that of Bi<sub>2</sub>Te<sub>3</sub>. Recent theoretical studies have also suggested that magnetic co-doping could facilitate enhancements in the ZT. For example, vanadium (V) has been shown via full-potential density functional theory to enhance ZT up to 28 percent for V concentrations up to 25 atomic percent in bulk niobium-doped strontium titanate (SrTiO<sub>3</sub>) [6]. In this study, co-doping was achieved by alternate ablation of vanadium or iron and Nb-doped SrTiO<sub>3</sub> targets. The samples were then annealed to enhance crystallinity. Our results suggest that co-doped films are single-phase.

#### 1.3 Scope of the Study

The focus of this research is on the discovery of oxide TE materials and devices for energy harvesting. Since the efficiency of  $SrTiO_3$ -based ceramics is relatively low, our research objective is to understand how doping and nanostructuring affects the electrical and thermal transport properties for energy harvesting applications. We plan to first, to synthesize doped oxide

thermoelectric materials for high temperature application. Second, to enhance and improve the figure of merit of the oxide by utilizing the low dimensionality effect. The co-doping with V and Fe will also be studied to understand the effect of magnetic enhancement on the electrical and thermal transport properties. Third, we will study the atomic-scale characterization (morphology). Fourth, since annealing has been shown to have an effect on the materials properties, we will study *in-situ/ex-situ* annealing using a TEM to capture live images during annealing. Fifth, measure the thermoelectric properties (electrical and thermal conductivity). Finally, model a thermoelectric device.

There are also several appendices to this study. Appendix A shows the derivation of the Fermi function [7], which allows us to physically describe the electrical conductivity and Seebeck coefficient. Appendix B shows the derivation of the Bose function, which allows determination of thermal conductivity [7]. Appendix C shows the derivation of the efficiency and figure of merit of the thermoelectric generator.

# **CHAPTER 2**

# LITERATURE REVIEW

# 2.1 <u>Thermoelectricity</u>

TE materials can be used to generate electricity from heat or extract heat from a system. The phenomena are known more specifically as the Seebeck and Peltier effects. For the Seebeck effect the input is heat and the output is electricity while electricity is the input for the Peltier effect and the output is cooling, which is called thermoelectric cooling (TEC). A schematic of a typical thermoelectric generator (TEG) is shown in Figure 2.1.



Figure 2.1- Thermoelectric generator (TEG)

Thermoelectric devices consist of a series of two dissimilar materials" referred to as p-type and ntype "called legs. These legs are connected in series by conductive materials. For TEG one side has high temperature  $T_h$  due to its close proximity to the heat source and the other side is called the heat sink due its close proximity to low temperature  $T_c$ . The temperature gradient causes the current to flow.

# 2.2 The Figure of Merit (ZT)

The efficiency of thermoelectric materials is measured by the thermoelectric figure of merit (ZT), which is defined as the following:

$$ZT = \frac{S^2 \sigma T}{k_{el}} \left( \frac{1}{1 + \frac{k_{ph}}{k_{el}}} \right)$$
(4)

where S is the Seebeck coefficient ( $\mu$ V/K) and  $\sigma$  is the electrical conductivity with units of (S/m),  $k_{ph}$  is the lattice thermal conductivity and  $k_{el}$  is the electronic portion of the thermal conductivity using units of (W/m-K) and T is the absolute temperature in (K). The ZT of the state-of-the-art Bi<sub>2</sub>Te<sub>3</sub> is ~ 1 at 300 K, which is still low for real applications from an economic view. Moreover, Bi<sub>2</sub>Te<sub>3</sub> is a toxic and volatile material and it is not suitable for high temperature applications. ZT should be ~ 3 for commercial purposes. The requirements for higher ZT have driven most of the research focus on how to enhance ZT. A semi-classical approach (Landauer- Boltzmann) will be used to enhance ZT. We used this approach since our research focuses on engineering of the materials properties at the nanoscale.

# 2.2.1 Electrical Conductivity

Someone may ask what causes the electrical current to flow. To answer this question we can use Figure 2.2, which is a schematic depiction of a simple elastic resistor. The electron can move from contact one to contact two without losing energy. If a small bias is applied, the current is proportional to the difference between Fermi energy as described in Eq. (5)



Figure 2.2 - One level TE device

$$I_{\text{one level}} = \frac{q}{t} (f_1(\varepsilon) - f_2(\varepsilon))$$
(5)

where q is the electron charge (1.6 e-19 Joules), t is the time it takes for an electrons to transfer from contact one to contact two and f(E) is the Fermi function as defined in Eq. (6).

$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T}}$$
(6)

By utilizing the density of states concept and noting that all energy channels conduct independently in parallel, we could write the current in an energy channel between E and E+dE [7] as described in Eq. (7).

$$dI = dE \frac{D(E)}{2} \frac{q}{t} (f_1(E) - f_2(E))$$
(7)

We only consider half of the density of states since only half of the channels carry electrons. Using Taylor series expansion the Fermi function around the equilibrium will be

$$f_1(\varepsilon) - f_2(\varepsilon) = \left[ -\frac{\partial f_0}{\partial E} \right] (E_{F1} - E_{F2})$$
(8)

For derivation of Eq. (8) see Appendix A. For a small bias  $E_{F1}-E_{F2} = qV$ . Using this fact and integrating, one can obtain the conductance of an elastic resistor as following:

$$\bar{\sigma} = \frac{I}{V} = \int_{-\infty}^{\infty} \left( -\frac{\partial f_0}{\partial E} \right) Z_E dE$$
(9)

$$Z_E = \frac{q^2 D(E)}{2t(E)} \tag{10}$$

where

Eq. (9) is valid for a degenerate material like a conductive metal wherein the Fermi energy is located a few KT above the energy range where the conduction function is non-zero [7]. On the other hand the derivation was based on an elastic resistor, which is not just ballistic. It may also extend to diffusive resistors as long as the energy is conserved and only momentum is changed. Since the time t is proportional to length for the ballistic regime and to  $L^2$  for the diffusive regime. One can rewrite Eq. (9) by utilizing the modified Ohm's law as described in Eq. (11) and the diffusion constant as described in Eq. (12)

$$R = \frac{\rho}{A}(L + mfp) \tag{11}$$

$$\bar{D} = \langle v_z^2 \rangle \tau$$
 and  $\lambda = \frac{2D}{\langle v_z \rangle}$  (12)

and since the relationship between the ballistic time and total time which is described by Eq. (13)

$$t = t_b \left( 1 + \frac{Lv_z}{2\bar{D}} \right) \tag{13}$$

then the conductivity will be described as following:

$$\sigma = \frac{q^2 D}{L} \frac{D}{\lambda} \{1, \frac{1}{W}, \frac{1}{A}\}$$
(14)

where the three items in the parenthesis correspond to1-D, 2-D and 3-D conductors [7]. To recap, the difference in the Fermi function causes the electrons to flow. Analysis of the Fermi function shows that applying a voltage will make a difference but also, the temperature gradient is responsible for the current. This is precisely what occurs in thermoelectric devices. The cold side held at low temperatures would change the Fermi function as shown in the Figure 2.3 while the hot side only has a small change as shown in Figure 2.3. The difference above the Fermi energy is positive with the one below the Fermi energy level being negative. The net difference is responsible for flow of the electrons from either to cold side for n-type or to the hot side for p-type. For a semiconductor, the location of the Fermi function band, the material is n-type on the other hand if the Fermi function is close to the valence band the material is p-type. The process might be controlled extrinsically by a process called doping, which involves the intentional addition of impurity atoms into the lattice of the material.



Figure 2.3 - Schematic depiction of the hot and cold contact effect on the Fermi function and the diffrence in Fermi function

# 2.2.2 Seebeck Coefficient

Seebeck concluded that the electrical field or "electromotive force"  $E_e$  is proportional to the difference in temperature by a constant S [V/K], using the same approach, one can rewrite Eq. (8) using a Taylor series expansion as following:

$$f_1(\varepsilon) - f_2(\varepsilon) = \left[ -\frac{\partial f_0}{\partial E} \right] (E_{F1} - E_{F2}) + \frac{\partial f}{\partial T (T_1 - T_2)}$$
(15)

The Fermi function can then be linearized, using the same approach as above and dividing the whole equation by 1/q results in:

$$\Delta V = \frac{1}{Z(E)} I - \frac{Z(S)}{Z(E)} \Delta T$$
(16)

where 
$$Z(S) = \int_{-\infty}^{\infty} \left(\frac{-\partial f_0}{\partial E}\right) \frac{E - E_F}{qT} Z_E dE$$
 (17)

then the Seebeck coeffecient assumes this form

$$S = -\frac{Z(S)}{Z(E)} = -\frac{E - E_F}{qT}$$
(18)

By examining Eq. (18), one can conclude to have a good Seebeck coefficieent we should choose the energy E to be far from the electrochemical potential (Fermi level)  $E_F$ , but that would lower the electrical conductivity.

# 2.2.3 Thermal Conductivity

Fourier's law of heat conduction  $q = -k\Delta T$  governs the heat transfer though a solid. The thermal conductivity k has two components  $k_e$  and  $k_L$ . For metals,  $k_e$  dominates the thermal transport, while for semiconductors  $k_L$  describes the manner that heat is transported in solids. One can simulate the bonding between atoms as a spring since they are not rigidly connected. Phonons are quanta of lattice vibrations due to the movement of heat through the material. Following the previous approach one can utilize the Bose function as given in Eq. (19). and Eq. (7). For dervation of Bose function see Appindix B.

$$B(\omega) = \frac{1}{1 - e^{\left(\omega \bar{h}\right)/k_B T}}$$
(19)

Since phonons are uncharged, we must replace q by hw. One can end up with the following:

$$I_{q} = \frac{1}{h} \int_{0}^{\infty} \left(\frac{M\lambda}{L+\lambda}\right)_{ph} \hbar \omega \left(B_{1}(\omega) - B_{2}(\omega)\right) d(\hbar\omega)$$
(20)

where M is number of mode that tell us the number of waves that fit into cross-section as describid in Eq. (21)

$$M = \frac{hDv}{2L} \left\{ 1, \frac{2}{\pi}, \frac{1}{2} \right\}$$
(21)

then

# 2.3 <u>Development of Thermoelectric Materials</u>

 $k = \frac{\pi^2 k_b^2 T}{3h} \left(\frac{M\lambda}{A}\right)_{nh}$ 

Researchers have spent several decades working to improve the efficiency of thermoelectric materials and devices. Recently, the economics of thermoelectric device technology has driven the investigations. It has been realized that even though the efficiency of state-of-the art thermoelectric materials is still low, the cost of the devices may be sufficiently low enough to justify realization of novel devices. The following is a summary of the developments of TE materials research.

# 2.3.1 Clasical Thermoelctric Materials

Despite the discovery of thermoelctricity by Seebeck in the 1800s, practical applications of the phenomenon were not realized until the mid 1950's. A radioisotope thermoelctric generator (RTGs) was developed by Mound Laboratories in Miamisburg, Ohio under contract with the United States Atomic Energy Commission. The project was led by Dr. Bertram C. Blanke [8]. The idea was to utilize a radioactive heat source (Pu238) combined with a thermocouple to generate electricity. Safety issues and low efficiency 3-7 percent, made the application limited to space missions. Soviet researchers in the Physical–Technical Institute (PTI)–led by A.F. Ioffe also developed a new concept of thermoelectricity that utilized the innovations derived from

(22)

semiconductor theory. Ioffe introduced the concept of the thermoelectric figure of merit (ZT). The charge carrier concentration for a good TE was determined to be  $(-10^{19} \text{ cm}^{-3})$  [9]. The PTI group tested more than thirteen hundred different materials, discovering only a few promising compounds, like Bi<sub>2</sub>Ti<sub>3</sub> and ZnSb. The devices suffered from low efficiency due to the interrelationship between Seebeck coefficient and electrical conductivity, namely, the coupling of the electrical conductivity to the electron thermal conductivity through the Wiedemann–Franz relationship as shown in Eq. (23)

$$k_e = L_0 \sigma T \tag{23}$$

where L<sub>0</sub> is the Lorenz factor ( $2.4 \times 10^{-8} J^2 K^{-2} C^{-2}$  for free electrons).

The decades that follow saw little progress in terms of thermoelectric materials and device research. However, recently, researchers have reported several high ZT compounds utilizing nanotechnology (thin film, nanowire, nanocomposite, etc.)

# 2.3.2 Advances in Thermoelectric Materiales

The research for thermoelectric materials, mainly follows two avenues either; form new materials that have a high power factor and low thermal conductivity or, utilizing the low dimensionality effect and its capability to decouple parameters that are used to determine the ZT (S,  $\sigma$ , k). The following is a brief summary of the recent new materials and the nano-scale approach.

# 2.3.2.1 Skutterudites (phonon glass-electron crystals)

In 1994 Slack introduced the concept of phonon glass-electron-crystals (PGEC), i.e., the best thermoelectric material should possess thermal properties similar to that of glass' 'amorphous structure' where phonons are scattered by the disordered structure resulting in lowering of the

thermal conductivity and electrical properties similar to single crystal materials where electrons flow with no scattering, which result in lowering of the electrical resistivity [10]. It turns out skutterudites fit these criteria. Skutteridites have unit cells with cubic structure AB<sub>3</sub>, A being Co, Rh or Ir and B being P, As and Sb. They have 32 atoms per unit cell, a large atomic mass, low thermal conductivity and high mobility. The reported ZT was about 1.3. Recently it has been reported that by utilizing a multiple fill different atoms to the unit cell, i.e., use four or more different elements in the skutteridite structure, ZT could be up to 1.6 due to lower thermal conductivity with no effects on the power factor [11].

# 2.3.2.2 Clathrates

"The clathrates are another group of compounds that have open structure into which loosely bound impurity atoms can be incorporated" [12]. It has two types. Type one refers to the conducting clathrate with general formula  $X_2Y_2E_{46}$ , whereas, type two is  $X_8Y_{16}E_{136}$ , where X and Y are the impurity atoms on two different sites and E is Si, Ge, or Sn [12]. Clathrates have low thermal conductivity due to the large number of host atoms in the unit cell. A figure of merit ZT as high as 1.35 at 900 K has been reported [13].

#### 2.3.2.3 Half-Heusler Alloys

Half-Heusler are alloys that are made of Ti, Zr or Hf. These materials are represented by X in half-Heusler formula XNiSn. These compounds have a high power factor at high temperature. They are n-type due to the high effective mass. Half-Heusler alloys are relatively easy to synthesize. They possess relatively high melting points ~1100 °C making them chemically stable at high temperatures [12]. The thermal conductivity of the typical half-Heusler compound is relatively high 10W/m K. "It assumed that most of the heat conduction is due to the acoustic-mode phonons because of their large group velocity" [12]. It has been reported that half-Heusler alloys have a figure of merit ZT as high as one at 700 K [14].

#### 2.3.2.4 Silicon-Germanium Alloys

Both of silicon and germanium possess a high thermal conductivity  $k_L$ , which makes them not suitable for thermoelectric applications. However,  $k_L$  is considerably reduced when solid solutions between the elements are formed. Silicon-germanium alloys are of particular interest for thermoelectric applications [15]. The composition of the alloy is normally ~30 percent silicon, and 40 percent germanium Si<sub>70</sub>Ge<sub>30</sub>. The band gap for silicon and germanium is 1.15 eV and 0.65 eV respectively. The thermal conductivity for the alloy is 10 W/m K while it is 113 and 63 W/m K for silicon and germanium respectively. The thermal conductivity is dramatically reduced in the alloy due to the grain boundary scattering [15]. Researchers have tried to utilize nanostructuring to enhance the ZT for these compounds. Figures of merit as high as 1.3 at 900°C have been reported for silicon-germanium nanocomposites [16].

# 2.4. Thermoelectricity and Low Dimensionality

Materials may be classified as 3-D for bulk materials, 2-D for ultra-thin films, 1-D for nanowires and 0-D for nanodots. Figure 2.4 shows the relationship between the density of states and energy as it changes with dimensionality. The energy is discrete at the quantum level, which means that the properties of the material vary as dimensionality is changed, i.e., a nanowire could have reduced thermal conductivity without reducing the electrical conductivity. Thin film superlattice materials consisting of multilayers of a few nanometer thin films or nanowires could scatter the phonon vibrations leading to low themal conductivity. This may arise because the phonon mode structure is affected by the low dimensionality [17]. The Seebeck coefficient might be enhanced in low- dimensional materials at a given carrier concentration. It has been reported that the thermoelectric power factor for a silicon germanium superlattice is higher than SiGe bulk materials [18].



Figure 2.4 - The density-of-state vs. energy for 0-D, 1-D, 2-D and 3-D materials.

#### 2.4.1 Embedded Nanoparticles

The idea of embedded nanoparticles is to have semiconductors with embedded semi-metallic or metallic nanoparticles aiming to lower the thermal conductivity and enhancing the power factor. The film might be fabricated by molecular beam epitaxy (MBE) or pulsed laser deposition (PLD). When the solubility limit is exceeded the semi-metallic nanoparticles start to form. The nanoparticles are normally on the order of 2-3 nm. It has been reported that in case of indium gallium arsenide (InGaAs) that adding three volume percent of these nanoparticles to the bulk semiconductor results in the thermal conductivity being reduced from five to three W/m K [19]. The lattice thermal conductivity is proportional to the mean free path of the phonon. Boundary and Umklapp scattering are the main two ways to lower the lattice thermal conductivity. Embedded nanoparticles add a third one, called impurity scattering which has played a big role in lowering the thermal conductivity due to the small size of the nanoparticles ~ 2-3 nm.

# 2.4.2 Thin Film Superlattices

Superlattice films are fabricated by depositing multiple layers of alternating films of different compositions in periodic stacks. The lattice mismatch, the electronic potential differences at the interfaces, the phonon electron interface scattering and the band structure modifications may lead to reductions in the lattice thermal conductivity without reducing the electrical conductivity [20]. It has been reported that the figure of merit ZT may be as high as 2.4 at room temperature for p-type  $Bi_2Te_3/Sb_2Te_3$  thin film superlattices with a period of ~ 6 nm [20]. Further investigation is still needed to develop commercial applications of the superlattice devices.

#### 2.4.3 Nanowires

Semiconductor nanowires may have reduced thermal conductivity without affecting the power factor, since the mean free path for electrons is different than the mean free path for phonons. The nanowire surfaces might be a means of blocking phonon propagation via the lattice. It has been reported that an efficient thermoelectric performance was obtained for a single component system of silicon nanowires with cross sectional areas of (10 nm X 20 nm) and (20 nm X 20 nm). By varying the nanowires size and the doping concentration, the ZT value of nanowire samples increased by two orders of magnitude over bulk Si [21].

# 2.5 <u>Thermoelectricity and Magnetism</u>

Recently, a new phenomenon has been observed, it is known as the spin Seebeck effect, which refers to the generation of spin voltage as a result of a temperature gradient [22]. When a magnetic material is subjected to a temperature gradient, it should generate different driving power of electrons in different spin channels [22] [23]. Figure 2.5 shows how the density of states of magnetic materials differs from that of non-magnetic materials.



Figure 2.5 - Density of states for a non-magnetic (left) and magnetic material (right).

Moreover, it has been reported that vanadium (V): niobium (Nb) co-doping of strontium titanate (STO) might enhance the figure of merit due to the local-polarization introduced by V ions [6].

The magnetism and its effect on thermoelectricity is still quite a new phenomenon that still needs to be better understood. We will study the growth, morphology and properties of V:Nb co-doped STO as an n-type TE material and Fe-doped STO as a p-type TE material.

#### 2.6 Oxide Thermoelectric Materials

The state-of-the-art thermoelctric materiales  $Bi_2Te_3$  and PbTe have been used to fabricate thermoelectric cooling devices. However, these materials are composed of toxic, rare and heavy elements that are not stable at high temperature [24]. Oxides have been disregarded as potential thermoelectric materials due to their poor electrical and thermal properties. Recently, researcher have reported that oxides have a potential as thermoelectric material.

#### 2.6.1 Layered Cobalt Oxides

"The layered cobalt oxides having the CdI2-type hexagonal CoO2 layer display decent thermoelectric properties mostly at high temperatures" [25]. "the layered structure consists of the NaCl-type [Bi2Sr2O4] layer and the CdI2-type CoO2 layer alternately stacked along the c-axis" [25]. "The layered structure works quite well in two ways. The one is that the electric current and the thermal current flow in different paths in space" [25][26]. "This allows us to control the lattice thermal conductivity by properly choosing the insulating block layer. This is a demonstration of electron-crystal and phonon-glass principle that was previously described" [25][27]. Moreover, The enhancement of the thermopower due to a small change in lattice parameter because of A site doping of ordered perovskite cobalt oxide  $Sr_3TCo_4O_{10.5}$  and  $R_{2/3}Cu_3Ti_{3.6}Ru_{0.4}O_{12}$ . These compounds have large entropies of mixed  $Co^{+3}/Co^{+4}$  states with low spin. A high ZT values of 1.2-2.7 have been reported for different cobalt systems [28].

#### 2.6.2 Zinc Oxide-Based Oxides

Zinc oxide (ZnO) is one of the most important thermoelectric materials and has extensive applications due to its unique properties such as high carrier mobility and Seebeck coefficient [29]. ZnO is a wide band semiconductor with a direct band gap of ~3.2-3.5 eV. Zinc has a relativly high electronegativity, resulting in the less polarizaed Zn-O bond [28]. Doping the zinc oxide with small amount of alumnium (Al) enhances the electrical conductivity more than three orders of magnitude at room tempreture, ZnAlO series thermoelectric conversion materials have large thermal conductivity  $\kappa$  about 40 W/mK at room temperature, thus the dimensionless figure of merit ZT remains around 0.3 at 1000°C [30].

# 2.6.3 Strontium Titanate-Based Perovskite-Type Oxides

Strontium titanate-based oxides have the ABO<sub>3</sub> cubic perovskite structure as shown in Figure 2.6. The physical properties are listed in Table I. They have the potential for use in high temperature applications due to the high melting point and high temperature stability, nontoxicity and power facter comparable to  $Bi_2Te_3$ . The main drawback is that the thermal conductivity is relativly high. Tuning of the electrical properties is possible by doping with elements that have different electron configuration than the host atoms that it replaces, which increases the carrier concentration and lowers the band gap. The doped oxide has the electrical characteristics of a semiconductor that can be either n-type or p-type. "Thus, although STO has a large  $S^2\sigma$ , the high k values of STO materials prohibit them from practical application"[24]. Approches that can more effectivily conquer lattice thermal conductivity k, including the introduction of low-dimensional configurations and

nanostructres, are desired [24]. In our research, we fabricated nanostructured "thin films" of V:Nb co-doped STO and Fe doped STO. Niobium  $(Nb^{5+})$  and vanadium  $(V^{5+})$  act as donors with additional magnetic effect for the vanadium. Iron  $(Fe^{3+})$  ions are believed to act as acceptors with possibility of spin Seebeck effect enhancement. Pulsed laser depostion (PLD) was used to fabricate the thin films. PLD has the capability to produce an epitaxial film with high electrical conductivity and low surface roughness [31] [32]. The formation of point defects is common during growth of oxide materials by PLD, therefore, controling the growth parameters (chamber pressure, substrate temperture and deposition rate) is extremely important and has a big impact on the materials properties. On the other hand, the growth procedure has the possibility to form what has been called "two dimensional electron gas" (2DEG). The 2DEG layers are separated by insulating dielectric layers (undoped STO). In the interlayers, the effective density of states is drastically increased, and as Seebeck coefficient is directly proportional to carrier concentration it too increases [33]. It has been suggested that this observation can be exploited in superlattice to have a net increase in Seebeck coefficient, and thus an increase in thermopower, with the theoretical result being a ZT of 2.4 at room temperature [33] [35].



Figure 2.6 STO cubic perovskite unit cell structure

Property	Value
Lattice parameter	0.3905 nm
Melting point	2080 °C
Atomic density	$5.12 \text{ g/cm}^3$
Dielectric constant	300
Thermal conductivity	12 W/m.K
Band gap	3.2 eV
Coefficient of thermal expansion	9.4E-6 Å/°C

Table I - STO PROPERTIES

# 2.7 Annealing and Thermoelectric Properties

Many materials properties depend on the structure of the material, i.e., an amorphous material may have different properties than single crystal or polycrystalline materials. Also, single crystals are anisotropic. For example, the modulus of elasticity for [100] copper is 66.7 GPa while for [111] copper it is 191.1 GPa [36]. Annealing is one of the most common approaches to improving the thermoelectric properties. It has been reported that the power factor for an annealed sample increased ~ 35% over that of the un-annealed sample [37]. In our research, we used the *in-situ/ex-situ* TEM annealing to study the change in morphology and its effect on the thermal transport properties.

#### 2.8 Rationale for Choice of Materials System

Ninety percent of the world primary energy is first converted to heat. The maximum efficiency of a typical fossil-fuel based technology is less than 40 percent resulting in more than 60 percent of the primary energy being lost as waste heat. Thermoelectric materials and devices have the potential to reclaim this waste heat. One of the the challenges facing the thermoelectric devices is the corrosive setting due to the high tempereture and high humidity operating conditions, i.e., power plants, vehicles, etc. Despite the low efficiency of the stae-of-the-art thermoelectric materiales like Bi<sub>2</sub>Te<sub>3</sub> and PbTe, these materials are composed of toxic, rare and heavy elements that are not stable at high tempereture. Oxides are known for their high temperature stability. Recently, niobium (Nb) doped strontium (STO) has been identified as a candidate n-type thermoelectric [23]. Nb:STO has a comparable power factor ( $S^2\sigma$ ) to Bi<sub>2</sub>Te<sub>3</sub> as shown in Table II.

Property	Bi <sub>2</sub> Te <sub>3</sub> (300 K)	20% Nb-STO (1000)
$S(\mu V/k)$	200	250
$\sigma (\Omega^{-1}.cm^{-1})$	10 <sup>-5</sup>	10 <sup>-4</sup>
K (W/m.k)	1.5	3
ZT	~1	0.37

Table II - PROPERTIES OF Nb:STO and Bi<sub>2</sub>Te<sub>3</sub>

The low figure of merit is primarily due to the relatively high thermal conductivity. Since The heat transfer through the oxides is mostly via phonons vibration. Scattering phonons may lower the thermal conductivity resulting in a higher ZT. Moreover a therotical study showed that V:Nb co-
doped STO may enhance the ZT due to the local spin-polarization [6]. Combining these materials with the nanoscale approach might lead to high ZT. On the other hand, to fabricate a device p-type and n-type legs are needed. Iron doped STO is a potential candidate for p-type doping with the possibility of the magnetism advantage.

## 2.9 Research Goal and Objectives

The focus of this research is on the discovery of oxide TE materials and devices for energy harvesting. Since the efficiency of the SrTiO<sub>3</sub>-based ceramics is relatively low our research goal is to understand how doping and nanostructuring affects the electrical and thermal transport properties for energy harvesting applications. We plan to first, synthesize doped oxide thermoelectric materials for high temperature application. Second, enhance and improve the figure of merit of the oxide by utilizing the low dimensionality effect. Third, the co-doping with V and Fe will also be studied to understand the effect of magnetic enhancement on the electrical and thermal transport properties. Fourth, we will study the atomic-scale characterization (morphology) including *in-situ/ex-situ* studies using a TEM to capture a life images during annealing. Annealing has been showing an effect on the materials properties. Finally, we will measure the thermoelectric properties (Seebeck, electrical and thermal conductivity).

## **CHAPTER 3**

### METHODS AND MATERIALS

#### 3.1 Pulesd Laser Deposition (PLD)

There are several ways to fabricate thin films. The two main methods are chemical vapor deposition (CVD) and its different types and physical vapor deposition (PVD) and its different types. Pulsed laser deposition (PLD) as shown in Figure 3.1 is one of the PVD methods. It consists of a high-powered excimer laser with wavelength in the UV range (157- 400 nm) and a PLD chamber. The laser ablates the target while it is simultaneously rastered and rotated.



Figure 3.1- Schematic of Pulsed Laser Deposition (PLD) system

This generates an expanding plasma that is referred to as the laser plume. The plume consists of atoms, molecules, and particulates from the target directed toward the substrate to form a thin film. To alter and control the growth rate, the number of laser shots and laser frequency must be specified. PLD has several advantageous features, it can use multi-components targets, multiple targets for multi-layer or alloy films, operate in controlled gaseous environments, variable substrate temperature, controllable growth rate and a high deposition rate. The disadvantages are that the deposition area is small (limited uniformity), the films might contain a particulates and the target composition might modified by ablation, which affects subsequent depositions. Prior to all PLD experiments, the chamber is cleaned with acetone and laboratory grad tissue paper. Substrates are prepared by sonication in a bath of acetone for 5 minutes followed by a bath of methanol, iso-propanol and de-ionized water respectively. Thin films of V:Nb co-doped STO and Fe-doped STO were grown by pulsed laser deposition (PLD).

## 3.1.1 Pulsed Laser Deposition Growth Rate Measurements

To measure the growth rate of Nb doped STO, a then film was deposited with twelve thousand pulses on the Nb:STO solid target. A cross sectional TEM sample was prepared followed by low magnification image to determine the thickness of the thin film. The film thickness was determined to be 680 nm as shown in Figure 3.2. The growth rate was calculated by dividing the thickness of the thin film by the number of pulses applied to the target during the growth of the film.

Growth rate = 680 nm/12000 pulse = 0.056 nm per pulse



Figure 3.2 - TEM image of the thickness of Nb:STO thin film/12000 pulse

# 3.2 Transmission Electron Microscopy (TEM)

Modern TEMs are among the most advanced tools for characterization of materials. The electron wavelength allows us to obtain sub-angstrom resolution. TEM can be combined with energy-dispersive x-ray spectroscopy (EDS), electron diffraction and electron energy loss spectroscopy (EELS). It would provide a complete morphological and compositional analysis of a material.

#### 3.2.1 Principle of Transmission Electron Microscopy

The smallest distance between two points that human eyes can resolve is 0.1-0.2 mm [38]. The resolution of the light microscopy is limited due to the wave length of the visible light (400-700 nm), according to the classical Rayleigh criterion for the light microscopy Eq. (24), or

$$d = \frac{0.61\lambda}{\mu \sin \alpha} \approx \frac{\lambda}{2NA}$$
(24)

where d is the smallest distance that can be resolved, i.e., the maximum resolution,  $\lambda$  is the wave length,  $\mu$  is the refractive index,  $\alpha$  is the semi-angle of the collection of the magnification lens and NA is the numerical aperture which is around one for vacuum and one and half for oil. It is clear, the high resolution is far from atomic level. To understand the materials and its properties a microscope with atomic-level resolution is a must. The electron wavelength depends on the accelerating voltage, i.e., for 300 KeV,  $\lambda$  is 0.0197 nm and for 100 eV,  $\lambda$  is 0.0040 nm, which is much smaller than the diameter of the atoms. The thickness of the sample should be less than 100 nm. When the incident high-energy beam interacts with the specimen, it produces a secondary signal as shown in Figure 3.2. The collection of the direct beam can be used to gather what is called a bright field image. The dark field image is produced by the collection of the scattered electrons. The images are usually captured by charged coupled device (CCD) camera. A diffraction pattern can be collected on the back focal plane to obtain useful information about the crystallography of the specimen. X-Rays can be used to collect information about the composition of the specimen by a technique called energy-dispersive x-ray spectroscopy (EDS). The inelastically-scattered electrons can be used for electron energy loss spectroscopy (EELS), which allows determination of stoichiometry and chemical information.



Figure 3.3 - Electron interaction with the specimen

## 3.2.2 Components of Transmission Electron Microscope

As shown in the Figure 3.4, the transmission electron microscope is composed of source of electrons called electron gun. The electron gun typically uses either a field emission source or a  $LaB_6$  thermionic emission source. The system also includes a couple of electromagnetic condenser lenses. The first lens is used to demagnify the image of the crossover and control the minimum spot size. The second one converges the beam at the specimen and controls the diameter of the illumination. The condenser aperture controls the intensity of the beam by allowing a certain fraction of the beam to interact with the specimen. The objective lens forms an inverted initial

image and determines the limit of the image resolution [38]. The objective aperture is placed by the back focal plan. It selects the electron that forms the image and improves the contrast. The magnification of the image is determined by the projector lens. A fluorescent screen allows the user to collect the electrons, which are then converted to light utilizing a thin scintillator. The light is then transferred to the CCD camera to capture the images.



Figure 3.4 - Schematic of the main components of the TEM

# 3.2.3 Transmission Electron Microscopy Sample Preparation

## 3.2.3.1 Cross Section Transmission Electron Microscopy Specimen

We used two methods to prepare samples for TEM imaging. The first method of sample preparation is cross-sections TEM specimen "conventional way" as shown in Figure 3.5. After cutting, 3x2 mm slices of the thin film are glued face-to-face at the film surface using M–bond adhesive. Mechanical grinding, polishing, lapping and dimpling are used to reduce the thickness down to ~20 microns. The samples are then ion milled by (Fishion, EAF 1010) to further reduce the thickness down to ~ 100 nm.



Figure 3.5 - Cross sectional TEM specimen

## 3.2.3.2 Plan View Transmission Electron Microscopy Sample

The first step is to cut a 3 mm disc from the substrate using the ultra sound cutter as shown in Figure 3.6. The substrate is then affixed to the aluminum mounting slide. The film faces a clear glass cover to insure the film will not get damaged during cutting. This is followed by mechanical grinding and polishing of the other side of the sample down to  $\sim$  40-50 microns, followed by dimpling the center of the sample down to  $\sim$  5-20 microns. The last step is thinning the interest area down to less than 100 nm by ion milling.



Figure 3.6 - Plan view TEM specimen

#### 3.2.3.3 Focused Ion Beam Microscopy (FIB)

The TEM sample shown in Figure 3.7 was prepared with high precision milling using focused ion beam (FIB). FIB sample preparation is composed of the following steps [39]: first, the deposit of the protective material onto the specimen surface in the selected area, i.e., a rectangular shape of platinum ( $15\mu$ mX \*1.5 $\mu$ mY) for around 200 nm thickness were deposited by electron beam using 2-5 KV, followed by depositing a rectangular shape of platinum ( $15\mu$ m X \* 1.5 $\mu$ m Y \* 1, 5 $\mu$ m Z), deposited by ion beam using 30 KV. Second, the extraction and rotation of the wedge containing the selected area, i.e., bulk-out around the sample using 30 KV, where the sample is tilted by 52 degree , followed by a U-cut around the sample, were the sample tilted back to 7 degree. The last step of preparation, After lift-out the sample by welding the sample to the tip of the probe then fix it to the TEM copper grid, final thinning and cleaning of the sample with low voltage using 5.0 KV



Figure 3.7- FIB/SEM for TEM sample prep.

## 3.2.4 Custom Transmission Electron Microscopy Ceramic Grid

The copper grid and M-bond adhesive are not suitable for *in-situ* TEM annealing. A novel specimen preparation technique was developed to facilitate TEM imaging. We used a ceramic bond and a handmade ceramic grid. The specimen preparation involves

- A. Make a 3 mm circular cut on the substrate by using the ultra-sonic cutter as shown in Figure 3.2.
- B. Mechanical grinding to 3 mm disc down to ~70-40 micrometer.
- C. Using the dimplier machine to make a one and half millimeter diameter hole (window) in the center of the grid then the grid is ready to use as shown in Figure 3.9.



Figure 3.8 - Custom TEM ceramic grid



Figure 3.9 - TEM cross sectional custom ceramic grid and ceramic adhesive

# 3.3 Scanning Transmission Electron Microsopic (STEM)

STEM is a type of transmission electron microscopy, it differs from conventional transmission electron microscope in that the electron rastered over the sample. STEM with a high angle detector has a resolution related to atomic number Z. It has two scanning modes. First, high-angle annular dark-field (HAADF), imaging depends on the thickness of the specimen and the atomic number of the elements. Second, annular bright field (ABF) does not depend on the atomic number. It has the capability to image light weight atoms like oxygen and nitrogen

## 3.4 Energy Dispersive X-Ray Spectroscopy (EDS)

Incident electrons excite and eject electrons from the inner shell of the atom forming a hole. An electron from the outer shell-or higher energy shell-will substitue to keep the equilibrium state. The extra energy will be released as an x-ray. The x-rays can be captured by an energy disperssive

spectrometer. Chemical analysis and quantification is possible since each element of the periodic table has a unique atomic structure that gives information about the composition of the specimen [40].

### 3.5 <u>X-Ray Photoelectron Spectroscopy (XPS)</u>

In 1921 Einstein was awarded the Nobel prize for his work on the photoelectric effect. Sixty years later Siegbahi received the Noble prize for his work on photoemission as an analytical tool (electron spectroscopy for chemical analysis (ESCA). ESCA is more commonly called x-ray photoelectron spectroscopy (XPS). It is a quantitative elemental analysis technique for solid surfaces. When a UV light or x-ray beam interacts with core of the atams ejecting a photoelectron with a certain kintic energy. One can calculate the binding energy according to the Eq. (25)

$$E_b = h\upsilon - (E_k + \Phi_f) \tag{25}$$

where  $E_b$  is the binding energy of the core electron, *h* is Planck's constant, v is the frequency of the the incoming quanta,  $E_k$  is the the kintic energy of the ejected electron and  $\Phi_f$  is the work function of the spectrometer. XPS is used to measure the elemental composition at the surface, and the chemical and electronic states. It also has the capability to measure the uniformity of the elemental composition near the surface by line mapping and the uniformity of the elemental composition as a function depth into the same using ion beam etching( depth profiling) [41]. Ultrahigh vacuum conditions are used during the meaurement to minimize the contamination of the surface. The output is a spectrum showing the binding energy verses intensity, i.e., number of electron per second (CPS). The data should be deconvoluted and compared to the database to identify the elements present and their oxidation states. Atomic fraction of the elements in multicomponent materials can be estimated utilizing the following equation:

$$A = \frac{I_A / F_A}{\sum I_n / F_n}$$
(26)

where A is the atomic percent, I is the intensity area and F is the sensitivity factor, which is materials dependent. To ensure the accuracy of the results the sample should be homogeneous and the materials surface should smooth and flat.

### 3.6 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) consists of the tip (probe) that scans the sample, a laser diode that shines the laser beam to the top of the canteliver beam to measure the deflection of the cantilever and a rant photo-detector as shown in Figure 3.10. AFMs usually have two modes: contact mode and noncontact mode. The samples were scanned in contact mode, which is utilized to scan the sample with the cantilever probe.



Figure 3.10 - AFM main components

A repulsive force deflects the cantilever beam. The deflection is measured by the laser and collected and converted into an image that represents the topoghraphy of the surface being scanned. AFM is capable of measuring the surface roughness as well as other physical problems depending on the applications used and the mode of operation.

#### 3.7 Physical Property Measurements System (PPMS)

The Quantum Design physical property measurements system (PPMS) has the capability to measure thermal conductivity k, Seebeck coefficient S and electrical conductivity  $\sigma$ , which allows calculation of the figure of merit ZT. For electrical conductivity, four terminals are placed on the top of the thin film, the terminals at the edge of the specimen were connected to a source of electric current (AC), the other two terminals are connected to a voltmeter as shown in Figure 3.11



Figure 3.11- PPMS four probe connection for electrical resistivity measurement

Since the resistivity is proptional to the length of the sample, Ohm's law can be used to calculate the electrical conductivity as described in Eq. (27) as

$$\sigma = \frac{1}{\rho} = \frac{L}{WT} \times \frac{I}{V}$$
(27)

where L is the length of the sample, W is the width and T is the thickness. The four probe measurement method has an advantage that it can eliminate the resistance of the terminal so it has no influence on the measurements. PPMS combined with thermal transport option (TTO) has the capablity to measure the thermal conductivity and Seebeck coefficient. To determine the thermal conductivity k, a stable time different gradient  $\Delta T$  over the sample must be established then one can calculate the thermal conductivity k as shown in Eq. (28).

$$k = \frac{I^2 R - P_{rad}}{\Delta T} - K_{shoe}$$
(28)

where the parameter P<sub>rad</sub> is estimated as follows:

$$P_{rad} = \sigma_t \left(\frac{S_a}{2}\right) \varepsilon \left(T_{hot}^4 - T_{cold}^4\right)$$
<sup>(29)</sup>

and K<sub>shoe</sub> is estimated as follows:

$$K_{shoe} = aT + bT^2 + cT^3 \tag{30}$$

and  $RI^2$  is the Joule heat generated by a heater of resistance R and current I.  $\sigma_t$  is Boltzmann constant = 5.7E -8 W/K<sup>4</sup>m<sup>2</sup>, S<sub>a</sub> is the sample surface area,  $\epsilon$  is the emissivity and a,b,c are constant given by the manufacturer.

# 3.8 Optical Profilometer

Optical profilers are an obstacle microscopes, it dedicated to measuring surface profile. By utilizing the light wavelength as a ruler, it has the capability to measure the surface roughness with high accuracy. [42] [43]. In this research, optical profilometer was used to measure the variation of the roughness due to the different annealing temperatures.

#### **CHAPTER 4**

#### NANOWIRES

#### 4.1 Introduction

Nanowires are one-dimensional materials. The physical properties of nanowires are different from bulk materials. Nanowires are predicted to show interesting properties for diameters less than 100 nm [44]. It has been demonstrated that using an iterative solution for Boltzmann transport to model the electronic transport that nanowires with diameters less than five nanometer are needed in order to obtain ZT greater than three [45]. The phonon component of thermal conductivity can be estimated as shown in Eq. (31)

$$k_{ph} = \frac{1}{3} C_V v_s \lambda \tag{31}$$

where  $C_v$  is the specific heat,  $v_s$  is the speed of sound in the materials and  $\lambda$  is the mean free path. If the diameter of the nanowire is equal or smaller than  $\lambda$ , then  $\lambda$  will be replaced by the size of the nanowire and the phonon thermal conductivity will be proportional to the size of the nanowire. It has been reported that silicon nanowires may have a high ZT ~ 1 compared to bulk Si due to the reduction of the thermal conductivity and optimizing of the carrier concentration at 200 K [21]. Moreover, it has been reported that PbTe nanowires have enhanced Seebeck coefficients and lower thermal conductivities [46]. Furthermore it has been reported that rough Si nanowires have low thermal conductivity due to the higher rate of diffuse reflection or back scattering of the phonons at the interface [47]. The measured ZT value of nanowires in many cases appears to be lower than the theoretical prediction [48]. Various fabrication techniques have been used: including sol-gel techniques, vapor-liquid-solid method (VLS) and template synthesis. Templates combined with PLD were used to fabricate Nb:STO nanowires [49].

#### 4.2 Nanowire Fabrication

Templates were written into 4 wt. % poly methyl methacrylate e-beam resists dissolved in anisole (PMMA-A4) using EBL (JEOL JBX-6300FS). The PMMA-A4 resist was coated onto single crystalline (100) oriented SrTiO<sub>3</sub> (STO) substrates (CrysTecGmbh). The PMMA-A4 was then spun on single crystal ceramic substrates at 3000 rpm for a final thickness of about 175 nm, and then baked for five minutes at 180 °C. Following the resist bake, a conductive polymer "ESPACER" was spun on and baked using the same speed and temperature. The patterns used trenches with horizontal widths ranging from 10 nm to one µm and lengths of 500 µm. After patterning; the resist was developed in a solution of methyl isobutyl ketone in isopropanol (MIBK) for one minute. The electron beam was set at a constant four nA current and 100 KeV accelerating voltage. Dose was manipulated along with pattern dimension and feature density to achieve the final templates. Template filling occurred under high vacuum (10<sup>-6</sup> Torr) at room temperature using PLD. A 248 nm wavelength KrF Excimer laser (GAM Laser EX 350) was used to ablate a SrTi<sub>.8</sub>Nb<sub>.2</sub>O<sub>3</sub> sintered target. Laser parameters were kept constant at two J/cm<sup>2</sup> with a repetition rate of five Hz. Following PLD the substrates were placed in an acetone bath at 90 °C for ten minutes and then sonicated for ten seconds. After the liftoff procedure, the substrates and nanostructures were annealed under high vacuum at 650 °C for one hour and then cooled at five  $^{\circ}$ C/min to room temperature. The sample was prepared for analysis by TEM by a previous student in the LORA group [49].

## 4.3 Results and Characterization

Atomic force microscopy, focused ion beam microscopy and scanning transmission electron microscopy (STEM/TEM) combined with energy dispersive x-ray spectroscopy were used to characterize the nanowires.

# 4.3.1 Atomic Force Microscopy Results

AFM results show that the nanowires appear to be  $\sim 100$  nm in diameter, based on a cross sectional profile as shown in Figure 4.1. Figure 4.2 shows that the nanowire of the same sample has some non-uniformity with  $\sim 45$  nm in diameter, which is smaller than what appears in Figure 4. the variation of the diameter might be due to some scumming in the photoresist



Figure 4.1- AFM image of Nb:STO nanowires



Figure 4.2- AFM image of nanowires with reduced thickness

## 4.3.2 Transmission Electron Microscopy Results

Conventional TEM sample preparation using micro polishing techniques are not applicable in our case due to the small feature size of our samples. Focused ion beam FIB, (FEI Helios Nanolab Dual Beam SEM/FIB), was used to extract specimens of the Nb-STO nanowire samples for TEM. Aberration corrected analytical microscopy (JEOL JEM-ARM200CF) combined with energy dispersive x-ray spectroscopy (EDS) and transmission electron microscope (TEM/STEM) were used for characterization. In contrast, high magnification TEM image show that the final dimensions is about ~ 60 nm as shown in Figure 4.3. Figure 4.4 is an HRTEM image of the Nb-STO nanowire, shows that the nanowire boundary is well defined and it has an epitaxial growth. Figure 4.5 shows a high-angle annular dark-field (HAADF) of the substrate (STO) and the Nb-STO nanowire. HAADF imaging depends on the thickness of the specimen and the atomic number of the elements, with higher atomic numbers producing higher intensity and brighter images

therefore rows with higher intensity represent A site Sr atoms and the lower intensity and less brighter represent B site Ti and Nb dopant.

These high intensity rows are spaced by 0.389 nm, which is in good agreement with the theoretical STO lattice parameter of 0.3905 nm. This image suggests that the niobium substitutes for Ti in the STO lattice. Moreover, Figure 4.5 shows that the interface contains a slight misfit dislocation core, due to structural relaxation.



Figure 4.3 - TEM high magnification images for the nanowires



Figure 4.4 - High-resolution image (HRSTEM) image of nanowire and substrate



Figure 4.5 - High-angle annular dark field (HAADF) image of nanowire and substrate



Figure 4.6 - (HAADF) image shows the Burger circuit

Also it shows that there are some defects like vacancies and Schottky defects as shown in the red box in Figure 4.5. Other researchers have observed similar types of defects [50]. The strain was calculated using the following formula, or

$$S = \frac{a_{film} - a_{bulk}}{a_{bulk}} \tag{31}$$

It showed that the strain is about 0.389 percent. The lattice parameter of the substrate is  $a_{bulk} = 0.3905$  nm, which is taken as the unstrained value.

The direction and the magnitude of the Burger vectors, was obtained by tracing a clockwise Burger circuit. It turns out the circuit is incomplete as shown in Figure 4.6.

Since annular bright field image (ABF) does not depend on the atomic number. It has an advantage compared to HAADF Therefore, it has the capability to image lightweight atoms like oxygen and

nitrogen. Figure 4.7 shows an annular bright field image of the Nb: STO specimen, the light dark circle is the oxygen atoms.



Figure 4.7 - ABF Atomic scale STEM of nanowire

Figure 4.8 shows a selected-area diffraction (SAD) pattern of Nb:STO nanowire and the substrate. It confirms that, the cubic structure of the STO and the nanowire. To calculate the lattice constant of the STO, the relationship below was used,  $dR = L\lambda$  where L is the camera length,  $\lambda$  is the electron wavelength for the 300 kV beam (0.0197 nm) and R is the distance between the direct diffraction spot (000) to the other diffraction spots. The calculated lattice parameter is 0.3885 nm, which is in good agreement with what was obtained from HRSTEM and the theoretical lattice parameter.

Furthermore, it confirms that the nanowires are epitaxial. Furthermore Figure 4.8 shows that, there is one-degree misalignment in the diffraction spots as indicated by the red parentheses, due to the structural relaxation.



Figure 4.8- SAD Pattern of the Nb:STO nanowire

## 4.3.3 Energy Dispersive X-Ray Spectroscopy Results

Figure 4.9 shows true area mapping of the nanowire, the mapping results suggests that the composition is 40 percent Sr, 54 percent Ti and six percent niobium. To confirm the results, EDS was performed on the target itself. It turns out that the weight percentage of the niobium is seven percent which is in a good agreement with the Nb:STO nanowire samples.

EDS line mapping shows that Nb is incorporated into the SrTiO<sub>3</sub> lattice by substituting for Ti as shown in Figure 4.10.



Figure 4.9 - True EDS mapping of the Nb:STO nanowire components



Figure 4.10 - EDS line mapping showing that Nb substitutes for Ti

# 4.4 <u>Summary and Conclusions</u>

The TEM results show that a well-defined, highly crystalline 60 nm Nb:STO nanowire was fabricated utilizing electron beam lithography to control the shape and the dimension and pulsed laser deposition. The samples were annealed after the deposition. Dislocation core were observed at the interface and the diffraction images of the nanowire overlapped with those of the substrate suggesting that the nanowires are epitaxial. The EDS mapping confirmed the stoichiometry of the nanowires. The line EDS suggests that the niobium substitutes for Ti in the STO lattice.

#### **CHAPTER 5**

## TEM STUDY OF ANNEALED Nb:STO THIN FILM

#### 5.1 Introduction

Experimental measurements on nanowires by other groups have shown that the ZT values appear to be lower than what has been predicted by the theoretical calculations. The charge carrier mobility of the nanowire is very low due to surface trap states and point defects [48]. Annealing can possibly reduce the defect density [51]. The nanowire samples in chapter four were annealed after deposition and lift-off because the polymer photoresist would degrade at the temperatures needed to form a single crystalline material. To understand how an annealing process affects the morphology of the thin film, TEM *in-situ/ex-situ* annealing processes were conducted to understand how the material crystallizes as the material was heated up to 700 °C.

#### 5.2 <u>Sample Fabrication</u>

The Nb-SrTiO3 thin film was deposited on SrTiO3 substrate at room temperature. The PLD system with a Coherent COMPexPro 201 KrF laser ( $\lambda = 248$  nm) is used, at a repetition frequency of 10 Hz, energy of 22 kV and 430 mJ with 5000 pulses. The target and substrate are kept at a distance of seven centimeters apart. Before deposition the substrates were cleaned by acetone, methanol, and isopropanol and deionized water, respectively. A cross sectional TEM sample was prepared, a custom ceramic TEM grid and ceramic adhesive were used as explain in section 3.2.4. A special TEM sample holder combined with a heater and cooling system was used to *in-situ* anneal the sample.

#### 5.3 Results and Characterization

Transmission electron microscopy was used to monitor the sample morphology during *in-situ* heat treatment of the samples. Life images and diffraction patterned were captured, EDS was used to study the annealing effects on the composition. An optical profilometer was used to study the roughness of the samples.

#### 5.3.1 In-situ Transmission Electron Microscopy Results

TEM coupled with *in-situ* annealing takes advantage of maintaining sample position and orientation compared to *ex-situ* heating followed by TEM imaging [52]. High temperature heat treatments are known to increase the crystallite size. Figure 5.1 shows a high-resolution TEM image of the sample showing the amorphous film deposited on the single crystal (100) STO substrate. Figure 5.2 shows high-resolution TEM images of the specimen at 400 °C, which is the temperature that the materials begins transitioning from amorphous to crystalline. The crystalline orientation of the film is the same as that of the substrate. Figure 5.3 shows a TEM image at 700 °C, the image does not show a clear high-resolution atomic scale images due to the high temperature effect, which results in high amplitude atomic vibrations. However, the image still shows separated crystalline and amorphous regions in the film. Figure 5.4 shows the film at room temperature after the annealing process, it shows that the film has only partially crystallized. Additional time is needed to produce a fully crystalline material. The results show that ordered stacking of the atoms starts at ~ 400 °C and it is dependent on the structure of the substrate. Figures 5.5 - A, B, C, D show the selected area electron diffraction pattern (SAED) at 300 °C, 400 °C, 500 °C and 700  $^{\circ}$ C respectively. They show how the atomic movement and vibration is increasing with increasing temperature.



Figure 5.1- TEM Image of amorphous thin film of Nb-STO for *in situ* annealing



Figure 5.2 - In-situ TEM annealed film at 400°C



Figure 5.3 - In-situ TEM annealed film at 700°C



Figure 5.4 - TEM Image of film after the *in-situ* annealing

#### 5.3.2 *Ex-situ* Annealing Results

Ex-situ annealing tests are conducted in order to find the temperature required to cause crystallization and to compare with the results of the *in-situ* TEM results. The thin films were imaged after deposition at room temperature and also after annealing at 350 °C, 550 °C and 700 °C. Each of the four samples consists of a SrTiO<sub>3</sub> substrate and a thin film of Nb:SrTiO<sub>3</sub> deposited at room temperature. The Coherent COMPexPro 201 F laser was used, at a frequency of 10 Hz, energy of 22 kV and 430 mJ with 5000 pulses on the Nb-SrTiO<sub>3</sub> to deposit the films. The target and substrate were kept at a distance of seven centimeter apart. Sample two (350°C anneal), was kept in the vacuum chamber after the deposition. Sample two required a total of 160 minutes; the temperature was raised to 350 °C in 30 minutes, kept at 350 degrees for 60 minutes, and given 70 minutes to drop down to room temperature. Sample three and four (550 °C anneal) required 200 minutes; the temperature was raised to 550 degrees in 30 minutes, kept at 700 degrees for 60 minutes, and given 110 minutes to drop down to room temperature. Sample four (700 °C anneal) requires 230 minutes; the temperature was raised to 700 degrees in 30 minutes, kept at 700 °C for 60 minutes, and given 140 minutes to drop down to room temperature. Figure 5.6 shows the annealed sample after heating at  $350^{\circ}$ , the amorphous film starts to crystallize slowly during the heat treatment. Figure 5.7 shows the annealed sample at 550 °C, which suggests that the film is completely crystallized. Figure 5.8 shows the annealed sample at 700°C, the film is fully crystallized with an increase in the number of the oxygen vacancies and Schottky defects.



Figure 5.5 - A, B, C, D-SAED pattern of the samples annealed *in-situ* at 300, 400, 500, 700 °C, respectively

The *in-situ/ex-situ* results show that, when the annealing temperature is below 400 °C, there is no crystallization of the Nb:STO amorphous thin film. The crystallization starts when the temperature approaches 400 °C. The crystallization is time dependent, i.e., the thicker the film the more time it takes to fully crystallize. Moreover, the results showed that the highest quality films were obtained when the annealing temperature is between 500-600 °C, when the annealing temperature is 700 °C, the film starts to have defects, i.e., oxygen vacancies and cationic vacancies. The results indicate that the Nb:STO might be stable for thermoelectric applications up to ~ 600 °C. Excess high temperatures might make the device unstable due to the increase in the number of defects that start to form. These defects might also lead to changes in the physical properties. Furthermore, extremely high temperatures might to diffuse the niobium to the surface, which might affect the physical properties of the thin film and the ZT value. To study how defects effects the performance of the thermoelectric device, *in-situ* characterization need to be conduct.



Figure 5.6 – *Ex-situ* TEM image of Nb:STO thin film annealed at 350 ℃



Figure 5.7 - *Ex-situ* TEM image of Nb:STO film annealed at  $550^{\circ}$ C



Figure 5.8 - *Ex-situ* TEM image of Nb:STO thin film annealed at 700 °C.
#### 5.3.3 Energy Dispersive X-Ray Spectroscopy Results

The EDS detector does function fat excessive annealing temperatures. To simulate the procedure, a 380 nm thin film was deposited on an STO substrate at room temperature. The sample was then divided into four pieces with one piece annealed at 350 °C, the second one annealed at 550 °C and the third one annealed at 750 °C. The samples were then quickly cooled to room temperature after each annealing treatment. Table III shows the composition of the samples at different annealing temperatures. Figure 5.9 shows the ratio of Nb to Sr in Nb doped STO thin film. It turns out that the ratio of Nb to Sr keeps increasing with increasing temperatures. This phenomenon might be due to an increase in the number of Schottky defects with increasing temperature. The ratio of Nb to Sr at room temperature is similar to that of the films annealed at 700 °C. Figure 5.10 shows the ratio of Ti to Sr in Nb-doped STO thin film. The ration of Ti to Sr also varies with temperature. The results shows that the composition is a function of temperature and the elemental ratios are not fixed which might have an effect on the material properties.

	W%	A%	W%	A%	W%	A%	W%	A%
	27 °C	27 °C	350 °C	350 °C	550 °C	550 °C	750 °C	750 °C
Sr	66.59	57.01	62.77	50.65	70.85	62.67	62.14	50.94
Ti	21.24.	33.14	29.98	43.84	19.37	29.00	27.25	41.14
Nb	10.95	9.85	7.25	5.51	9.31	8.32	10.60	8.22

TABLE III - EDS RESULTS Nb:STO THIN FILM AT DIFFERENT ANNEALING TEMPERATURES



Figure 5.9 - The weight ratio of Nb to Sr in Nb doped STO

annealed at different temperatures



Figure 5.10 - The weight ratio of Ti to Sr in Nb doped STO annealed at different temperature

Defects might be the cause of the change in the composition with temperature. Since Nb:STO contains more than two kinds of ions, defect of each ion may occur. The two type of defects are Schottky defects, which are defined as cation vacancy-anion vacancy pairs the other type is Frenkel defects, which are defined as cation vacancy and cation interstitial pair [36]. To understand what cause the composition ratio to change with temperature the number of Schottky and Frenkel defects were calculated utilizing the following equations:

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right) \tag{32}$$

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$
(33)

Where  $Q_s$  and  $Q_{fr}$  are the energy required to form the Schottky and Frenkel defects, respectively, k is Boltzmann's constant, T is the absolute temperature and N is the total number of atomic sites, which can calculated by utilizing Eq. (34), where N<sub>A</sub> is Avogadro's number (6.02 E23 atoms/mol),  $\rho$  is the density of the material and A is the atomic weight of the elements

$$N = \frac{N_A \rho}{\sum A_E} \tag{34}$$

Table IV shows the energy required to form the various types of defects in STO [53]. Table V shows how the number of Schottky and Frenkel defects per meter cube changes with increasing annealing temperature. The results show that the number of defects is a function of the different annealing temperatures.

Defect reaction	Defect energy(eV per defect)
SrO Schottky	1.53
TiO Schottky	2.48
Strontium Frenkel	3.94
Titanium Frenkel	7.10
Oxygen Frenkel	2.57

# TABLE IV - SCHOTTKY AND FRENKEL DEFFECT FORMATION ENERGIES IN SrTiO3

# TABLE V- NUMBER OF SCHOTTKY AND FRENKEL DEFECTS/ $\mathrm{m}^3$

Temp.	Ns-Sr	Ns-Ti	N <sub>Fr</sub> -Sr	N <sub>Fr</sub> -Ti	N <sub>Fr</sub> -O
°C	defect/m <sup>3</sup>				
RT	7.5423 E15	7.2231 E7	-	-	6.0626 E7
350	2.5685 E22	4.5484 E18	4.1598 E12	-	7.8598 E18
550	7.6382 E23	1.2409 E21	3.0831 E16	1.2028 E7	2.6284 E21
750	6.0300 E24	3.7785 E22	7.0140 E18	2.1258 E11	9.0547 E22

The calculation shows that the most prevalent defect in STO is expected to be strontium-oxygen Schottky defect ~  $6.0300 \text{ E}24 \text{ m}^{-3}$ . Figure 5.11 shows the calculated ratio of Ti/Sr defects with increasing temperature. For the case of Frenkel defects, the results suggest that the main defect would be the oxygen defect. Oxygen vacancies are the main issue that must be surmounted to realize p-type STO, since they act as n-type dopants. This calculation suggests that the oxygen vacancies might compensate for the p-type impurity to change the dominant carrier type from p-to n-type.



Figurer 5.11- The ratio of Ti/Sr Schocttky defect vs. Temp.

The attractive energy between the SrO Schottky defects (cation and anion vacancies pair) were calculated utilizing Eq. (35), which was used to estimate the Coulombic force between two charged entities:

$$E = \frac{-e^2}{4\pi\varepsilon\varepsilon_0 r} \tag{35}$$

where r is the distance between the cation and anion (0.3812 Å), e is the electronic charge (1.6020 E-19 C),  $\varepsilon$  is the dielectric constant 300 and  $\varepsilon_0$  is the permittivity of a vacuum (8.85 E -12F/m). The attractive energy is 12.1511 kJ/mole, which is 0.1259 eV, which means that they are not free to move due to the attractive force. However, if the thermal energy due to the temperature gradient  $E = K_B T$  is higher than this attractive force then the defect will start to move. The cation site vacancy is a negative charge with respect to the lattice and it is positive for the anion site with respect to the lattice.

## 5.3.4 Analysis of Surface Roughness

An optical profilometer was used to measure the roughness and morphology of the same samples that were previously discussed. The results showed that the roughness increased with temperature. For the room temperature sample, the roughness was 6.65 nm as show in Figure 5.12. For the sample annealed at 350 °C the roughness is 16.37 nm as shown in Figure 5.13. For the 550 °C sample the roughness is 30.05 nm as shown in Figure 5.14. For the 750 °C sample, the roughness varies from ~ 91 nm as shown in Figure 5.15. The root mean square roughness is 9.08 nm, 28.98 nm, 43.55 nm and 143.22 nm respectively. The RT and 750 °C samples possess irregular shapes, i.e., a non-uniform surface with pits with depths similar to that of the film thickness as shown in Figure 5.12 and 5.15.

#### Surface Stats:

Ra: 6.65 nm Rq: 9.08 nm Rt: 155.13 nm

#### Measurement Info:

Magnification: 20.48 Measurement Mode: PS Sampling: 820.31 nm Array Size: 368 X 240

Surface Stats:

Ra: 16.37 nm

Rg: 28.98 nm

Rt: 1.43 um



Figure 5.12 – Three dimensional interactive display of RT  $^{\circ}$ C annealed Nb:STO film and its roughness



Figure 5.13 – Three dimensional interactive display of 350 °C annealed Nb:STO film and its roughness



Figure 5.14 – Three dimensional interactive display of 550 °C annealed Nb:STO film and its roughness

Surface Stats:

Ra: 30.85 nm

Rg: 43.55 nm

Rt: 1.17 um



Figure 5.15 – Three dimensional interactive display of 750 °C annealed Nb:STO film and its roughness

#### 5.4 Conclusion

A custom TEM ceramic grid was made to facilitate the first *in-situ* TEM annealing study of Nb-STO up to 700 °C. The results were validated by an *ex-situ* TEM annealing study up to 750 °C. The results showed that the best annealing temperature for Nb:STO is about 500-600 °C and the annealing process should be performed with oxygen to minimize the oxygen vacancies in the film. EDS composition analysis for different temperatures showed that the composition is a function of temperature. The roughness is also a function of temperature, the higher the temperature the higher the roughness.

#### CHAPTER 6

# MORPHOLOGY AND PHYSICAL TRANSPORT PROPERTIES OF V:Nb CO-DOPED STO THIN FILMS

## 6.1 Introduction

Complex oxides are excellent candidates for use in thermoelectric (TE) energy harvesting devices. The key challenge is optimization of the TE figure of merit (ZT). Despite the high thermal conductivity present in most oxides, the power factor ( $S^2\sigma$ ) of materials like doped SrTiO<sub>3</sub> rivals that of bismuth telluride. Recent theoretical studies have suggested that magnetic co-doping could facilitate enhancements in the ZT. For example, vanadium (V) has been shown via full-potential density functional theory to enhance ZT up to 28 percent [5] for V concentrations up to 25 atomic percent in bulk niobium-doped strontium titanate (SrTiO3).

#### 6.2 <u>Sample Fabrication</u>

Thin films of vanadium V:Nb co–doped STO were grown by pulsed laser deposition (PLD) to study the effect of vanadium co-doping of Nb:STO films. The PLD system with a Coherent COMPexPro 201 KrF laser ( $\lambda = 248$  nm) is used, at a repetition frequency of 10 Hz, energy of 22 kV and 430 mJ. The target and substrate are kept at a distance of five centimeters apart. The experimental parameters used to produce the samples are shown in Table VI. The samples were grown on different substrates LAO, STO, MgO and fused silica with different doping concentrations. The samples were annealed at 700 °C in high vacuum (~10<sup>-5</sup> Torr) and in the presence of oxygen (~10<sup>-2</sup> Torr).

Sample	Film	Substrate	No of laser	No of laser	Deposit	Deposition	With
No			pulses on Nb: STO	pulses on V target	ion Temp.	pressure Torr	<b>O</b> <sub>2</sub>
			target		°C		
25	V:Nb -	MgO	50 * 65	250 *65	700	1.6 E-2	Y
	STO						
26	V:Nb -	LAO	50* 65	250*65	700	1.7 E -2	Y
	STO		STO				
			250*65 Nb				
37	V:Nb -	LAO	200 * 50	1000 *50	700	5.5E-5	N
	STO						
63	V:Nb -	STO	100*25	1000* 25	700	2.5E-5	N
	STO						
64	V:Nb -	Fused	100*25	1000* 25	700	2.5E-5	Ν
	STO	Silica					

TABLE VI - V:Nb Co-DOPED STO THIN FILMS PLD PARAMETERS

# 6.3 Results and Characterization

Scanning transmission electron microscopy, x-ray photoelectron spectroscopy, energy dispersive x-ray spectroscopy results and physical properties measurements system were used to characterize morphology and electrical and thermal transport properties of the thin films.

## 6.3.1 <u>Scanning Transmission Electron Microscopy Results</u>

The growth parameters for sample 37 are given in Table VI. Figure 6.1 - A, B is a high-resolution TEM image of the V:Nb co-doped STO thin film. The TEM study suggests that the films are highly crystalline. Misfit dislocations arise due to the difference in the interatomic spacing between film and substrate. Figure 6.2-A shows a misfit dislocation present at the film/substrate interface as shown in the red box.



Figure 6.1 - A, B Cross-sectional STEM images of the V: Nb co-doped STO thin film (sample # 37)

For sample 63 which is the one the transport measurement was conduct on, the TEM data suggests that the film is polycrystalline with point defects as shown in Figure 6.2 - A, B. Figure 6.3 shows the SAED pattern of sample 63



Figure 6.2 - A, B Cross-sectional TEM images of the V:Nb co-doped STO thin film (sample # 63)



Figure 6.3 – SAED pattern of the V:Nb co-doped STO thin film (sample #63)

### 6.3.2 X-Ray Photoelectron Spectroscopy Results

The XPS results for sample 25 suggest that, there is no evidence of metallic phases due to precipitation of the V or Nb dopants. The oxidation states for V:Nb co-doping STO are  $V^{5+}$ , Nb<sup>5+,</sup> Sr<sup>2+</sup> and Ti<sup>4+</sup> as shown in Figure 6.4. The atomic percentage for the respective elements was found to be 25.96 for Sr, 18.45 for Ti, 2.33 for Nb, 3.65 for V and 49.59 for O. The XPS composition results represent the topmost 10 nm of the surface of the thin film, so the composition of the entire film may be slightly different than what indicated by XPS



Figure 6.4 - XPS photoemission peaks for V:Nb co-doping STO thin film

## 6.3.3 Energy Dispersive X-Ray Spectroscopy Results

The PLD parameters of sample 63 are shown in Table IV. It is the sample that thermal transport measurements conduct on. Figure 6.5 shows that the EDS weight percentage of the elements. The atomic percentage of the samples was found to be 46.29 for Sr, 37.63 for Ti, 4.15 for Nb and 11.93 for V.



Figure 6.5 – EDS composition W% Of V: Nb co-doping STO thin (sample # 63)

## 6.3.4 Transport Property Measurements of the Samples

Transport property measurements (PPMS) were used to measure the electrical conductivity of V:Nb co-doped STO thin film samples. The growth parameters of the samples are shown in Table VI.

#### 6.3.4.1 Electrical Conductivity Measurements

Figure 6.6 shows the room temperature measurements of the sheet resistivity of the sample 63. It was in order of 10 E-4  $\Omega$ -m. The electrical conductivity is the reciprocal of the resistivity. The result suggests that the conductivity is one order of magnitude above the state-of-the-art Bi<sub>2</sub>Te<sub>2</sub>. The conductivity might be further tuned by changing the carrier doping concentration. Further study into this system has been suggested for future work.



Figure 6.6 - PPMS resistivity measurements of V:Nb co - doped STO thin film

#### 6.3.4.2 Seebeck Coefficient Measurements

Transport property measurements (PPMS) were also used to measure the Seebeck of V:Nb codoped STO Thin Film samples. Figure 6.7 shows the Seebeck results for sample 63. The result shows that the Seebeck coefficient is -22.5  $\mu$ V/K, which is too low to be considered for thermoelectric device applications. Candidate thermoelectric materials should have a Seebeck coefficient in order of ~150  $\mu$ V/K. The negative sign is also an indication that the film is n- type.



Figure 6. 7 - PPMS Seebeck coefficient measurements of V:Nb co-doped STO thin film

#### 6.3.4.3 Thermal Conductivity Measurements

Transport property measurements (PPMS) was also used to measure the thermal conductivity of V:Nb co-doped STO Thin Film samples. The thermal conductivity is ~ 4.7 W/K-m as shown in Figure 6.8. However, PPMS measurements are not an accurate means of measuring thermal conductivity since the value obtained is for the sample as a whole (substrate and thin film). It is not easy to distinguish between the film conductivity and the substrate. A future work would use a different measurement approach for more accurate result.



Figure 6.8 - PPMS thermal conductivity measurements of V:Nb co-doped STO thin film

## 6.4 Conclusion

Vanadium niobium-doped strontium titanate thin films were successfully fabricated by PLD system. XPS results showed that the oxidation state of the vanadium is  $V^{5+}$  and the niobium is Nb<sup>5+</sup> the results showed no evidence of metallic precipitation. EDS results the composition of the co-doped thin films. TEM/STEM results showed that the crystalized V:Nb co-doped STO thin film. PPMS results showed that the Seebeck coefficient is on the order of 25  $\mu$ V/K and the electrical resistivity is on the order of 1E-4  $\Omega$ -m, which indicates that the carrier concentration needs to be optimized.

#### **CHAPTER 7**

# MORPHOLOGY AND PHYSICAL TRANSPORT PROPERTIES OF IRON DOPED STO THIN FILM

#### 7.1 Introduction

Both p-type and n-type legs are needed to fabricate a thermoelectric generator. STO p-type has not been reported due to the compensation effect mainly caused by the oxygen vacancy [54]. Nevertheless, p-type STO will make a big impact on the oxide semiconductor materials. It would open a wide window of application, i.e., thermoelectric devices, a wide band gap semiconductor diode, protonic conductors for electrochemical application, etc.  $Fe^{3+}$  is a possible acceptor as trivalent ions on Ti<sup>4+</sup> with the added advantage of magnetism for spin Seebeck effect.

#### 7.2 Sample Fabrication

To study the effect of iron doping of STO thin films of Fe doped STO were grown by pulsed laser deposition (PLD) on LAO, STO and fused silica substrates, respectively with different concentrations. The PLD system with a Coherent COMPexPro 201 KrF laser ( $\lambda = 248$  nm) is used, at a repetition frequency of 10 Hz, energy of 22 kV and 430 MJ. The target and substrate are kept at a distance of five centimeters apart. The samples were annealed at 700 °C in high vacuum (~10<sup>-5</sup> Torr) and in the presence of oxygen (~10<sup>-2</sup> Torr). The sample growth parameters are shown in detail in Table VII.

#### 7.3 <u>Results and Characterization</u>

Scanning transmission electron microscopy, x-ray photoelectron spectroscopy, energy dispersive x-ray spectroscopy results and physical properties measurements system were used to characterize the thin films.

Sample	Film	Substrate	No of	No of	Deposition	Deposition	With
No			pulse	pulse	Temp.℃	P. Torre	$O_2$
			Fe	STO			
31	Fe:STO	STNO	500*50	100 *	700	2.2 E-2	Y
STEM				50			
22	Fe:STO	MgO	1500*95	50*95	700	3.7 E-2	Y
XPS							
66	Fe:STO	STO	1500*25	200*25	700	5.2 E-5	N
PPMS							
43	F:STO	LAO	750*50	150*50	RT	2.3 E-2	Y
PPMS							
78	Fe <sub>2</sub> O3:STO	LAO	100*50	100*50	650	4.3 E-5	N
PPMS							
79	Fe:STO	Fused	500 *99	50 *99	650	4E-5	N
PPMS		Silica					

# TABLE VII - PLD PARAMETERS OF Fe – STO THIN FILMS

# 7.3.1 <u>Scanning Transmission Electron Microscopy Results</u>

The STEM images for sample 31 show that the perovskite structure is retained in nanostructured Fe-doped  $SrTiO_3$  and Fe is incorporated into the STO structure. The STEM results suggest that the

films are epitaxial and that there is no evidence for metallic precipitation as shown in Figure 7.1. The Fe-doped STO thin films were grown by (PLD) with different number of laser pulses, i.e., 1000 pulses for Fe and 100 pulses for STO with 25 repetitions. The STEM image shows that the sample consists of alternating regions of Fe-doped STO and undoped STO. This is due to the alternating ablation of the respective PLD targets. The growth procedure creates a two-dimensional electron gas Fe-doped STO and STO.



Figure 7.1- A, B Cross-sectional HAADF and ABF STEM images show the Fedoped STO thin film with different doping concentration region

## 7.3.2 Energy Dispersive X-Ray Spectroscopy Results

The EDS analysis for sample 31 confirms that Fe is incorporated into the nanostructures by substituting for Ti sites as indicated by Figure 7.2. The atomic compositions percentages are 40.66 Sr, 23.78 Ti, 4.43 Fe and 41.14 O. EDS line mapping shows that Fe substitute for Ti as shown in Figure 7.3.



Figure 7.2 - EDS spectrum for Fe:STO thin film



Figure 7.3 - EDS line mapping for Fedoped STO thin film

## 7.3.3 X-Ray Photoelectron Spectroscopy Results

The XPS results for sample 22 show that, there is no evidence of metallic Fe. The oxidation state for iron is  $Fe^{2+}$  60 percent <sup>and</sup>  $Fe3^+$  40 percent as shown in Figure 7.4. Figure 7.5 shows the oxidation state for  $Sr^{2+}$  and  $Ti^4+$ . The atomic compositions percentages are 24.13 for Sr, 19.85 Ti 13.19 Fe and 42.82 O.



Figure 7.4 - XPS photoemission Fe peaks of Fe-doped STO thin film



Figure 7.5 - XPS photoemission Ti and Sr peaks of Fe-doped STO thin film

## 7.3.4 Transport Properties Measurements of the Samples

The PPMS was used to measure the electrical, thermal conductivity and the Seebeck of Fe:STO thin film samples.

#### 7.3.4.1 Electrical Conductivity Measurements

The growth parameters of the samples are shown in Table VII. Figure 7.6 shows the room temperature measurements of the sheet resistivity of the sample number 66. The resistivity is ~10 E-3  $\Omega$ -m. The electrical conductivity is the reciprocal of the resistivity. The result shows that the conductivity is kind of high which indicates that the carrier doping concentration is low, since the electrical conductivity is proportional to carrier doping concentration.



Figure 7.6 - PPMS resistivity measurements of Fe doped STO thin film

## 7.3.4.2 Seebeck Coefficient Measurements

Figure 7.7 shows the room temperature measurements of the Seebeck coefficient for sample 66. The results suggest that the Seebeck coefficient is -650  $\mu$ V/K, which is too high for thermoelectric devices. The negative sign indicates that the film is n-type.



Figure 7.7 - PPMS Seebeck coefficient measurements of Fe doped STO thin film.

## 7.3.4.3 Thermal Conductivity Measurements

The thermal conductivity measurements suggest that the thermal conductivity is on the order of 8.5 W/K-m as shown in Figure 7.8. The PPMS measurements are not accurate since it measures the conductivity for the substrate and the film. It is not easy to distinguish between the film's thermal conductivity and that of the substrate.



Figure 7.8 - PPMS thermal conductivity measurements of Fe doped STO thin film

# 7.4 Conclusion

Iron doped strontium titanate was successfully fabricated by PLD system. XPS results showed that the oxidation states of the Iron are Fe<sup>3+</sup> and Fe<sup>2+</sup> 60% to 40% respectively, the results showed no evidence of metallic precipitation. TEM/STEM results showed that the crystalized Fe doped STO thin films consist of separate doped and undoped regions, which can be exploited to create a two- dimensional electron gas in Fe doped STO and STO. PPMS results showed that the Seebeck coefficient is ~ -600  $\mu$ V/K and the electrical resistivity in order of 1E-3  $\Omega$ -m, which indicates that the carrier concentration needs to be optimized.

#### **CHAPTER 8**

#### THIN FILM THERMOELECTRIC POWER GENERATOR

## 8.1 Introduction

To realize applications for novel thermoelectric materials, it is necessary to fabricate a thermoelectric generator. Thin film thermoelectric generators have an advantage due to their small size, which might open a wide window for future applications. TEGs contain of a series of p-n type legs. The output voltage of the device may be expressed as

$$V_{out} = n(S_P - S_N)\Delta T \tag{36}$$

The figure of merit of thermoelectric generator can be expressed as

$$Z_G = \frac{(nS)^2 G_G}{R_G} \tag{37}$$

where  $G_G$  is the thermal resistance of the thermopile and  $R_G$  is the electrical resistance of the thermopile. The efficiency can be expressed as

$$\eta = \frac{P}{Q} = \frac{\Delta T}{2T_M + \frac{\Delta T}{2} - \frac{4}{Z}}$$
(38)

For the derivation, see Appendix C.

Examining Eq. (38) one can conclude that  $\Delta t$  and Z are the main two factors to optimize the thermoelectric device.

## 8.2 Design of Thermoelectric Modules (TEG)

To design an efficient thermoelectric generator, the geometry should be optimized based on the properties of the thermoelectric material. The legs were designed as shown in Figure 8.1. The TE device was designed to have hot side, while the other side is cold as shown in Figure 8.2.



Figure 8.1 – Schematic of thermoelectric n-p legs for TEG



Figure 8.2 – Schematic depiction of TEG fabricated by PLD and 3-D printer

## 8.3 Fabrication of Thermoelectric Generator

To fabricate thermoelectric modules, a 3-D printer combined with the PLD system was used. The 3-D printer was used to fabricate two polymer masks to control the deposition as shown in Figure 8.3. The modules consist of V:Nb doped STO as an n-type leg and Fe-doped STO as a p-type leg. Two TE modules were fabricated, the first one, was fabricated on amorphous fused silica substrate as shown in Figure 8.4 and the second, was fabricated on a (100) single crystal STO substrate as shown in Figure 8.5. V:Nb-STO and Fe-doped STO were deposited respectively, as n-and p-type

legs. The film was then annealed at 700 °C, to enhance the crystallinity of the film. To ensure the Ohmic-contact, silver paint with zero resistivity was uesd to connect a gold plated copper wires to the legs. Two types of thermocouple were uesd to measure the temperature by the hot and cold sides.



Figuer 8.3 - Masks made by 3-D printer



Figure 8.4 - Thermoelectric device on fused silica substrate



Figure 8.5 - TEG fabricated on (100) single crystal STO substrate

## 8.4 <u>Results</u>

A temperature gradient of ~100 °C was maintained. For the thermoelectric module that fabricated on (100) STO substrate, the voltmeter reading was ~18 mV and the one that was fabricated on fused silica, the voltmeter reading was ~ 29 mV. This is sufficient to generate power in the micro-Watt range, which can be used for personal electronics. The voltmeter is not good enough to masure the resistivity and the current. More sophisticated instruments are a must for accurate results.

#### **CHAPTER 9**

#### **CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK**

#### 9.1 <u>Conclusions</u>

This study represents the first experimental demonstration of thin films of Fe-doped STO and V co-doped Nb: STO fabricated by PLD. STEM and TEM show that epitaxial single crystal thin films were produced with the desired doping. EDS mapping indicates that V and Fe substitutes for Ti in the STO lattice. XPS results show that the oxidation state for iron is  $Fe^{2+}$  and  $Fe^{3+}$ , the oxidation states for V co-doping Nb:STO are V<sup>5+</sup>, Nb<sup>5+</sup> Sr<sup>2+</sup> and Ti<sup>4+</sup> and that there is no evidence for metallic Fe, V or Nb exists. Physical properties measurements were used to measure the electrical conductivity, thermal conductivity and Seebeck. The results showed a high Seebeck coefficient and low electrical conductivity for the Fe doped STO thin film. This indicates that the carrier concentration is low. Increasing the carrier concentration will lower the Seebeck coefficient and increase the electrical conductivity; optimization between them is a must. For the vanadium niobium co-doped strontium titanate films, the Seebeck coefficient is low and the electrical conductivity of thin films.

The *in-situ/ex-situ* annealing study showed that the film starts to crystallize at 400 °C. Annealing temperatures of 500 - 600 °C are the best temperatures to form a crystal film. To minimize oxygen vacancies, oxygen should be introduced during the annealing process. Schottky defects were found to be the most common defects. The temperature also influences the roughness of the films. The results show that the composition is also a function of temperature.

For the nanowire characterization the results showed that, Nb-doped nanostructures were fabricated with a minimum size of  $\sim 60$  nm. An annealing heat treatment was used to produce perovskite nanostructures similar to the substrate. The EDS results suggest that the nanostructure dopant concentration is identical to that of the solid target. The EDS line mapping showed that Nb substitutes for Ti in the STO lattice.

#### 9.2 Recommendations for Future Work

The first priority should be investigation of the effect of oxygen concentration on the doping of Fe doped STO thin film, i.e., optimize the carrier concentration, measure Hall Effect, consider supperlattice structure for low- k. It is also important to utilize film sensitive methods to measure thermal conductivity like  $3\omega$  or laser flash techniques and to measure the electrical conductivity by four probe method.

Superconducting quantum interference device (SQUID) and other magnetic characterization are also recommended to identify the role of spin on the thermoelectric material. Similar optimization processes are recommended for the V:Nb co-doped STO films.

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# Appendix A[7]

## Fermi Function Derivative

$$f(x) = \frac{1}{e^x + 1} \quad \text{where } x = \frac{E - E_f}{kT} \quad \text{utilizing chain rule}$$
$$\frac{\partial f}{\partial E} = \frac{df}{dx} \frac{\partial x}{\partial E} = \frac{df}{dx} \frac{1}{kT} \quad (1)$$
$$\frac{\partial f}{\partial E_f} = \frac{df}{dx} \frac{\partial x}{\partial E_f} = -\frac{df}{dx} \frac{1}{kT} \quad (2)$$

$$\frac{\partial f}{\partial T} = \frac{df}{dx}\frac{\partial x}{\partial T} = -\frac{df}{dx}\frac{E - E_f}{kT^2}$$
(3)

From Eqs. (1), (2), and (3)

$$\frac{\partial f}{\partial E} = -\frac{\partial f}{\partial E} \tag{4}$$

$$\frac{\partial f}{\partial T} = -\frac{df}{dE} \frac{E - E_f}{T}$$
(5)

Utilizing Taylor series expansion.

$$f(E, E_f) \approx f(E, E_0) + \left(\frac{\partial f}{\partial E}\right)_{E=E_0} (E - E_0) \quad (6)$$

From Eq. (5)

# Appendix A (continued)

$$\left(\frac{\partial f}{\partial E}\right)_{E=E_0} = \left(-\frac{\partial f}{\partial E}\right)_{E=E_0} \tag{7}$$

By letting f(E) stand for  $f(E, E_f)$  and  $f(E_0)$  stand for  $f(E, E_{f_0})$  someone can write

$$f(E) \approx f_0(E) + \left(-\frac{\partial f_0}{\partial E}\right)(E - E_0)$$
 (8)

Rearranging

$$f_1(E) - f_2(E) = \left[ -\frac{\partial f_0}{\partial E} \right] (E - E_0)$$
(9)

Which is as same as Eq. (7) in chapter 2

# Appendix B[7]

# Bose Function Derivation

$$n(x) = \frac{1}{e^x - 1},$$
 (1)

where 
$$x = \frac{h\omega}{kT}$$
 (2)

Utilizing chain rule 
$$\frac{\partial n}{\partial T} = \frac{dn}{dx} \frac{\partial n}{\partial T}$$
 (3)

$$\frac{\partial n}{\partial T} = -\frac{h\omega}{kT^2} \frac{dn}{dx}$$
(4)

$$\bar{h}\,\omega\frac{\partial n}{\partial T} = -\frac{kx^2}{dx}\frac{dn}{dx}\tag{5}$$

$$=\frac{kx^{2}e^{x}}{(e^{x}-1)^{2}}$$
(6)

# Appendix C

Derivation of Thermoelectric Generator Efficiency

$$\eta = \frac{P}{Q} \tag{1}$$

$$P = \frac{\left(\Delta V\right)^2}{4R} = \frac{\left(S\Delta T\right)^2}{4R} \tag{2}$$

$$Q = Q_F - Q_J + Q_{P^{\circ}} \tag{3}$$

$$Q = (k_n \frac{A_n}{l_n} + k_p \frac{A_p}{l_p})\Delta T - \frac{1}{2}I^2(\rho_n \frac{l_n}{A_n} + \rho_p \frac{lp}{Ap}) + SIT_H$$
(4)

$$I = \frac{S\Delta T}{2(\rho_n \frac{l_n}{A_n} + \rho_p \frac{lp}{Ap})}$$
(5)

then

where

$$\eta = \frac{P}{Q} = \frac{\Delta T}{2T_M + \frac{\Delta T}{2} - \frac{4}{Z}}$$
(6)

$$Z = \frac{S^2}{\left(\left(k_n \rho_n\right)^{0.5} + \left(k_p \rho_p\right)^{0.5}\right)^2}$$
(7)

#### Name RIAD ALZGHIER

Prof. Experience: Process Engineer, Intel Corporation, Aloha, Oregon, as of August 2014.

#### **Education**:

Ph.D. in Mechanical Engineering: University of Illinois at Chicago (UIC)
3.64/4.0 GPA
Research Area: Nanofabrication of Complex oxide Material, Thermoelectric material and devices
Dissertation Title: Synthesis and Atomic-Scale Characterization of Oxides
Thermoelectric Materials and Devices

Master of Science in Mechanical Engineering: University of Illinois at Chicago (UIC) 3.55/4.0 GPA Dec. 2010 Concentration Area: Computational Mechanics, Multi-body Dynamics, Finite Element Methods

Bachelor of Science in Mechanical Engineering: Mu'ta University, Al Karak, Jordan 1999

#### Publication:

<u>Riad A. Alzghier</u>, Jeremiah T. Abiade, Gordon H. Waller, Robert F.klie, Nanofabrication and Atomic-level Characterization of Complex Oxides for Energy Application. To be submitted <u>Riad A. Alzghier</u>, Jeremiah T. Abiade, Sara Krysik, Robert F.klie *In-situ/ex-situ* Annealing TEM Characterization for Nb Doped STO Thin Films To be submitted Riad A. Alzghier, Jeremiah T. Abiade, Robert F.klie, Patrick Co-Doping to Enhance the Thermoelectric Figure of Merit of Titanate Thin Films. To be submitted <u>Riad A. Alzghier</u>, Jeremiah T. Abiade, Robert F.klie, Patrick Morphology and Thermal Transport Properties of Iron Doped STO Thin Films. To be submitted

#### Conference

- R. Alzghier and J. Abiade, "Nanofabrication and Atomic-level Characterization of Complex Oxides for Energy Application" Material Science & Technology, Conference & Exhibition (MS&T'12), Pittsburgh, Pennsylvania, USA \_ 2012
- R. Alzghier and J. Abiade, "Atomic-Scale Characterization of Nb-Doped for Energy SrTiO<sub>3</sub> Nanostructures for Energy Harvesting and Application" TMS, 142<sup>nd</sup> Annual meeting & Exhibition, San Antonio, Texas, USA\_2013
- R. Alzghier and J. Abiade and R. klie "Magnetic Co-doping of Niobium-doped Strontium Titanate Thin Films for Energy Harvesting Applications" Material Science & Technology, Conference & Exhibition (MS&T'13) Montreal, Quebec Canada\_ 2013
- R. Alzghier and J. Abiade, R. klie and P Phillip. "Co-Doping to Enhance the Thermoelectric Figure of Merit of Titanate Thin Films". Material Research Society, MRS Fall Meeting & Exhibit\_2013
- R. Alzgheir, K.-B. Low, Q. Qiao, R. Klie and J. Abiade. "Nanofabrication and Atomic-Scale Characterization of Heavily Doped Complex Oxide" Nanomaterials for Energy, GRC, Ventura, CA, 2013

### Skills

- Pulsed Laser Deposition (PLD)
- Transmission Electron Microscopy (TEM/STEM)
- Scanning Electron Microscopy (SEM) & (EDS)
- Focus Ion Beam Microscopy(FIB)
- Electron Beam Lithography (EBL)
- Photoelectron Spectroscopy(XPS)

#### Computer skills

Pro/ENGINEER, ABAQUS, ANSYS, MATLAB, and Microsoft Word/Excel

#### Professional Experience:

#### Teaching (TA)

- Mechanical Engineering Design of Machine Elements.
- Computer Aided Design (Pro/Eng. And ABAQUS)
- Manufacturing Process Principles
- Engineering Dynamics

#### Mechanical Engineer

Star Factory, 2001-2003 Amman, Jordan

- Head of production maintenance department, responsible for ensuring production continuity of the plant
- Managed 30-40 full time employees (eight mechanical engineers, thirty technicians)
- Improved the quality and the quantity of the production, utilizing the time effectively, and reduce the human error by a continuous educational and training courses for the employee
- Ensured adherence to production schedules

#### Mechanical Engineer

Al Mawared Factory, 1999-2001, Sahab, Jordan

- Responsible for maintenance department activities which included; repair, calibrations and assembling of variety of plant production machinery
- Ensured adherence to maintenance schedules
- Implemented process improvements to production process which resulted in higher quality and efficiency
- Trained technicians in maintenance tasks

#### Professional Society Association:

- Material Science And Technology (MS&T)
- Minerals, Metals & materials Society (TMS)
- Material Advantage
- American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE)
- American Society of Mechanical Engineering (ASME)
- Arab American Association Of Engineering & Architects (AAAEA)