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Nitride Thin Films for Thermoelectric
Applications:
Synthesis, Characterization and Theoretical
Predictions

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به نام خداوند جان و خرد کنیزم برتر اندیشه برگزید

خداوند نام و خداوند جای خداوند روزی ده رهنمای

شاهنامه فردوس

In the name of the lord of both wisdom and mind

To nothing sublimer can thought be applied

The lord of whatever is named or assigned

A place, the sustainer of all and the guide

The Persian epic "The Book of Kings"

Abu 'l-Hasan Ferdowsi Tusi

10th century A.D.

Abstract

Thermoelectrics is the reversible process which transforms a temperature gradient across a material into an external voltage through a phenomenon known as the Seebeck effect. This has resulted in niche applications such as solid-state cooling for electronic and optoelectronic devices which exclude the need for a coolant or any moving parts and long-lasting, maintenance-free radioisotope thermoelectric generators used for deep-space exploration. However, the high price and low efficiency of thermoelectric generators have prompted scientists to search for new materials and/or methods to improve the efficiency of the already existing ones. Thermoelectric efficiency is governed by the dimensionless figure of merit zT , which depends on the electrical conductivity, thermal conductivity and Seebeck coefficient value of the material and has rarely surpassed unity.

In order to address these issues, research conducted on early transition metal nitrides spearheaded by cubic scandium nitride (ScN) thin films showed promising results with high power factors close to $3000 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 500°C . In this thesis, rock-salt cubic chromium nitride (CrN) deposited in the form of thin films by reactive magnetron sputtering was chosen for its large Seebeck coefficient of approximately $-200 \mu\text{V/K}$ and low thermal conductivity between 2 and $4 \text{ Wm}^{-1}\text{K}^{-1}$. The results show that CrN in single crystal form has a low electrical resistivity below $1 \text{ m}\Omega\text{cm}$, a Seebeck coefficient value of $-230 \mu\text{V/K}$ and a power factor close to $5000 \mu\text{Wm}^{-1}\text{K}^{-2}$ at room temperature. These promising results could lead to CrN based thermoelectric modules which are cheaper and more stable compared to traditional thermoelectric material such as bismuth telluride (Bi_2Te_3) and lead telluride (PbTe).

In addition, the project resulting this thesis was prompted to investigate prospective ternary nitrides equivalent to ScN with (hopefully) better thermoelectric properties. Scandium nitride has a relatively high thermal conductivity value (close to $10 \text{ Wm}^{-1}\text{K}^{-1}$), resulting in a low zT . A hypothetical ternary equivalent to ScN may have a similar electronic band structure and large power factor, but with a lower thermal conductivity value leading to better thermoelectric properties. Thus the elements magnesium, titanium, zirconium and hafnium were chosen for this purpose. DFT calculations were used to simulate TiMgN_2 , ZrMgN_2 and HfMgN_2 . The results show the MeMgN_2 stoichiometry to be stable, with two rivaling crystal structures: trigonal NaCrS_2 and monoclinic LiUN_2 .

Preface

This thesis is prepared for my Licentiate defense and is a part of my PhD studies at the Thin Film Physics Division (Energy Materials Unit) of the Department of Physics, Chemistry and Biology (IFM) at Linköping University. The aim of this thesis is to synthesize and study novel nitride semiconducting thin films (i.e., cubic chromium nitride) and to simulate hypothetical ternary compounds which have prospective thermoelectric properties.

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During the course of research underlying this thesis, I was enrolled in *Agora Materiae*, a multidisciplinary doctoral program at Linköping University, Sweden.

List of included papers

Paper I

Microstructure and Thermoelectric Properties of Chromium Nitride Thin Films

M. A. Gharavi, S. Kerdsonpanya, S. Schmidt, F. Eriksson, N. V. Nong, J. Lu, C. Pallier and P. Eklund

Manuscript in final preparation

Author's contribution:

I planned and coordinated the experiments, and performed all of the depositions. I characterized the samples with SEM and XRD, and participated in the TEM, AFM and thermoelectric characterization. I summarized the data and wrote the manuscript.

Paper II

Theoretical Studies on MeMgN₂ Superstructures (Me = Ti, Zr, Hf)

M. A. Gharavi, R. Armiento, B. Alling, P. Eklund

Manuscript in final preparation

Author's contribution:

I was part of the project planning and discussions. I performed the calculations and wrote the manuscript.

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1. Introduction

Energy efficiency and greenhouse gas reduction stress the need for alternative sources of power generation. One logical approach would be to directly harvest waste heat and to transform it into electrical energy. For this, thermoelectrics can be used. Thermoelectric devices have many industrial applications such as waste heat recycling produced from internal combustion engines and power generation for wearable electronics to name a few. This is due to the Seebeck effect which is the conversion of a thermal gradient across a device into an external voltage. The opposite operation, the Peltier effect, induces a thermal gradient when an electric current is passed through the thermoelectric device. This property can be used for refrigeration without the need of a coolant.

The heart of thermoelectric research is to enhance device efficiency, which is done by maximizing the dimensionless figure of merit, zT :

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \quad (\text{eq. 1})$$

where α is the Seebeck coefficient, $\sigma = 1/\rho$ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. The Carnot engine efficiency is obtained when zT reaches infinity. By maximizing the power factor ($\alpha^2 \sigma$) and minimizing thermal conductivity, the efficiency of a thermoelectric device will increase. However, today's thermoelectric devices have a relatively low zT value of approximately unity, as these three parameters are interdependent. In addition, usage of traditional thermoelectric material includes other challenging aspects as well. Bi_2Te_3 and PbTe are well known thermoelectric materials, but the low production of tellurium plus the use of toxic elements limits them to niche applications. This includes solid state cooling for specialized optoelectronics devices, radio isotope thermoelectric generators used for deep space exploration and prospective military applications.

To go beyond this, new thermoelectric materials can be engineered according to the phonon glass – electron crystal (PGEC) approach¹, i.e., designing materials where charge carriers will flow freely as in a crystal, but the lattice contribution to thermal conductivity is disrupted much like phonon scattering in glass. Nanostructuring, doping, alloying and synthesis

of multilayers and superlattices, can simultaneously decrease thermal conductivity and electrical resistivity, resulting in higher zT values.

Another method to approach the problem of finding novel thermoelectric material is to utilize first principles calculations by predicting hypothetical semiconducting ternaries for thermoelectrics. It is assumed that compared to a binary, equivalent ternaries composed of heavy elements should have a similar electronic band structure but with a lower thermal conductivity, thus the crystal structure would be more effective in phonon scattering without hindering the charge carrier conduction. Such theoretical methods coupled with modern computers will allow fast simulations of an equivalent ternary to any known binary semiconductor. By constructing phase diagrams and choosing any hypothetically stable compound for band structure calculations, experimentalists can with a much higher degree of confidence choose appropriate material systems for research.

Interest in the research in this thesis started with cubic scandium nitride (ScN). It is known that ScN² has an approximate power factor of $3000 \mu\text{Wm}^{-1}\text{K}^{-2}$, which is high for an early transition metal nitride mainly known for high temperature hard coating applications. However, its relatively high thermal conductivity prevents its use as a thermoelectric material in pure form. Experimental research continued by synthesizing cubic chromium nitride (CrN) thin films. These thin films are deposited by reactive magnetron sputtering, which have the benefit of good control over the crystal quality and phase purity of the films. In addition magnetron sputtering is also suitable for synthesizing metastable material and superlattices, allowing a wide range of sample modification and synthesis. CrN is a well-known hard coating with good high temperature mechanical and chemical stability. Thermoelectric measurements (discussed in paper I) have shown Seebeck coefficient values of $-230 \mu\text{V/K}$. Under-stoichiometric single crystal CrN films are shown to have a resistivity below $1 \text{ m}\Omega\text{cm}$ resulting in power factors close to $5000 \mu\text{Wm}^{-1}\text{K}^{-2}$ at room temperature. In addition, CrN has a low thermal conductivity of approximately $2 \text{ Wm}^{-1}\text{K}^{-1}$ which is attributed to the localized $3d$ orbitals which give the electrons large effective masses and consequently low thermal conductivity.

The research revolving around this thesis emphasized on two main characteristics to improve the thermoelectric properties of CrN: enhancement of crystal quality for maximum electrical conductivity and

introducing metallic Cr_2N phase impurities in the form of nanoinclusions. In addition, scandium nitride (ScN) was chosen as an appropriate thermoelectric group three nitride for simulating a hypothetical semiconducting ternary. By using density functional theory (DFT), it is possible to predict a hypothetical equivalent ternary composed of group two alkaline earth and group four early transition metal nitrides. If successful, such ternaries could be synthesized experimentally and tested for any potential thermoelectric properties.

2. Thin film synthesis and characterization

Synthesis of nanostructured materials can be done by many techniques. For example, synthesis and fabrication by ball milling and electrodeposition have shown to be suitable for scaling up to the industrial level while being affordable and easy to handle. On the other hand, versatile methods such as molecular beam epitaxy and pulsed laser deposition which can prepare precise samples in 0D, 1D and 2D morphologies are usually more complicated and expensive, and are suitable for laboratory research. Some techniques are both cheap enough for industrial scale mass production while at the same time capable of producing research-quality samples. Sputter deposition is one of these methods. This section discusses the basics of sputter deposition and some of the concepts in utilizing the technique.

Diode sputter deposition

Sputter deposition was first reported by W. R. Grove³ in the year 1852 but it took several decades for it to reach much use. The basic concept of sputter deposition is based on momentum transfer. Similar to a game of pool, a high energy incident particle will hit the surface of any desired material, ejecting the source or “target” atoms (figure 1). The ejected particles will be transported through the deposition chamber and eventually condense on the substrate. What makes sputtering attractive for research and industry is that the synthesis procedure is usually done far from thermodynamic equilibrium, and metastable materials can be synthesized.

The sputtering yield for a specific working gas is defined as the number of ejected target atoms per incident particle (normally a noble gas ion) which is usually between 0.1 and 3. The sputtering yield is related to the energy and incident angle of the bombarding ions, the relative masses of the ions and target atoms, ambient pressure, and the surface binding energy of the target atoms^{4 5}.

Figure 1. Incident ions will collide with the target material and eject the surface atoms. Particle energy and mass, incident angle and ambient pressure all play key roles in how the target surface will be affected.

For sputter deposition, a vacuum chamber is required (figure 2). The created vacuum is needed to remove any residual gases, especially water vapor, which can deteriorate the synthesis process by oxidation. The maximum vacuum attainable by the system is known as the base pressure. However sputtering requires a steady flow of the sputtering gas, which will amount to a constant working gas pressure. A too low working gas pressure will prevent the plasma from igniting. A too high working gas pressure will result in more target material to be sputtered for the deposition, but will also thermalize the sputtered species, losing their energy. As the distance between the target and substrate is kept at a constant, thermalized particles will go through a random walk process and the mean free path will be small, hindering nucleation at the surface. Particles in a working gas pressure of 4.5 mTorr will have a mean free path of approximately 1 cm.

A noble gas is used as the sputtering gas for inertness. As momentum transfer is most efficient when the mass of the target atoms and the working gas are similar, argon gas is used for most targets as it is cheap, abundant and suitable for most materials, although a gas mixture with neon (for light element sputtering) or krypton (for heavy element sputtering) could be used.

Figure 2. High vacuum DC magnetron sputtering chamber “Adam”. Base pressure is 2×10^{-7} mBar. A base pressures at this level would have an approximate particle mean free path of 250 m. Note the installation of two magnetrons (plus computer controlled shutters) utilizing two separate targets. Photo by the author.

In order to ionize the argon gas and guide the ions towards the target, an electric field is utilized with the target material acting as the negative terminal (the cathode) and the chamber walls acting as the positive terminal (the anode). A stray free electron is accelerated by the electric field from the cathode towards the anode. When the electron reaches the first ionization energy of argon (15.7 eV), a direct hit with an argon atom will ionize the atom and eject another electron:

Eventually, the result will be an avalanche of electrons constantly ionizing argon gas which themselves will start to feel the electric field and be attracted towards the cathode. The outcome of a direct impact with the target surface will be sputtered atoms and secondary electrons. The sputtered atoms will travel to the substrate and if the distance between the target and substrate and the mean free path of the atoms are optimized, a thin film will deposit on the substrate. On the other hand, the secondary electrons will again enter an “avalanche” process to continuously form positive argon ions. The discussed mechanism is known as diode sputter

deposition which utilizes an electric field and a self-sustaining plasma (a mixture of positive ions, electrons, and neutral atoms) for the deposition process. The self-sustainability of the plasma can be visually confirmed by the plasma glow which is the result of the recombination of an argon ion with an electron, and emitting visible light (figure 3).

Figure 3. Pure argon plasma glow from the HV duel magnetron sputtering system "Adam". Photo by the author.

Today, diode sputtering is generally considered obsolete (however, it is still used for sputtering targets with magnetic properties). A high working pressure of 100 mTorr is needed for the plasma to remain self-sustaining (as the probability of an impact between the electron and the argon atom is low) and these gas pressures greatly decrease the mean free path of the ejected atoms resulting a very slow deposition rate with a low film uniformity. The utilization of a magnetron will allow lower working pressures (approximately 1-10 mTorr) while self-sustaining the plasma.

Magnetron sputtering

The magnetron consists of two or more permanent magnets stationed behind the target with opposite poles sided next to each other and water-cooled to insure that their temperature will remain below the Curie temperature. The

generated magnetic field will trap the secondary electrons forcing them to move in a helical motion along the field lines, increasing the electronic mean free path near the target (and ionization process of the working gas) before being absorbed and allowing lesser working pressures for the deposition process. The physics behind this phenomenon can be described by the Lorentz force:

$$\mathbf{F} = q_e (\mathbf{E} + \mathbf{v} \times \mathbf{B}) = m_e \mathbf{a} \quad (\text{eq. 3})$$

The electric and magnetic fields will cause a helical motion (figure 4).

Figure 4. The “right hand law” will force the electron to move in circles in presence of a magnetic field. The spiral movement will increase the mean free path of the electrons.

A sputtering system that includes a magnetron is known as a magnetron sputtering system (figure 5). The disadvantage of a magnetron sputtering system is that only a fraction of the target that is located in between the magnets is sputtered (the target “race track”).

Methods have been devised to reduce waste. Target providers usually accept and recycle expensive metallic targets for a lower resale price and industrial scale sputtering systems incorporate revolving cylindrical or very

large rectangular targets with an optimized magnet configuration for maximum target utilization.

Figure 5. Schematic diagram of a target installed above a magnetron. Magnetron sputtering has the disadvantage of etching only a fraction of the target material known as the “race track”. Photo by the author.

The strength of the magnetic fields of the inner and outer magnets can either be equal (balanced) or non-equal (unbalanced) which is shown in figure 6. Balanced magnetrons fully confine the plasma near the target surface while in the unbalanced configuration magnetic field lines deviate from the center, covering a larger area. The result will be that the plasma will extend to include the substrate. The argon ions will affect the growth of the thin film and can enhance the film quality. Substrate bias is also used in order to utilize argon ions for the growth process as a negative bias will attract argon ions towards the growing film. One can regulate the bias voltage and use this mechanism to ion etch and clean the substrate and remove physisorbed contaminants or to influence the growing film (adhesion, nucleation, crystal structure, and texture) by choosing an appropriate bias and form different film qualities ranging from highly defective polycrystalline films with small grain sizes to highly textured large grained films. If the bias of the substrate is positive, electron heating occurs, but typically in a non-uniform and uncontrollable fashion.

Figure 6. Magnetrons in the balanced (left) and unbalanced (right) configuration.

The sticking coefficient is temperature dependent. Too low temperatures will hinder surface diffusion and adatom mobility, which will disrupt the layer formation. On the other hand, too high temperatures will result in re-evaporation of different atoms. Decreasing the substrate temperature will allow deposition on temperature sensitive substrates and will also decrease the amount of energy required for the process.

Magnetron sputtering systems deposit different materials in both the form of pure elements and/or solid solutions. For alloys, one can sputter the desired material from an alloy target. However, the sputtering yield of the constituents of the alloy target can be an issue. As the sputtering yield for any given target atom is different, the constituents of the alloy target will sputter at different rates which may disrupt film stoichiometry. For example, in a hypothetical AB alloy system, element A may deplete as it has a higher sputtering yield while a surplus amount of element B will remain. As time passes equilibrium will form (high sputtering yield for element A vs. higher concentrations for element B) and stoichiometry will be preserved leading to the conclusion that alloy sputtering is a self-sustaining process as long as the target is conditioned initially before starting the deposition process.

For a compound target (oxide, nitride, etc.) the ejected particles are usually not of compound nature (metal oxide/nitride molecule). Also the sticking coefficient of the electronegative element is likely to be lower, resulting sub-stoichiometric films⁶. Compounds may have very low sputtering yields which is why reactive sputtering is used instead.

Reactive sputtering

In reactive sputtering, a reactive gas is included in the gas flow to form nitrides and oxides (and carbides, oxynitrides, sulfides, etc.). The molecules/ions of the reactive gas will combine with sputter deposited atoms and form the compound material. However, the reactive gas may also react with the target material and “poison” the target by creating an oxide/nitride film with a new sputtering yield. The deposition process will continue with a poisoned target, but because the sputtering yield decreases, the film formation time on the substrate will increase resulting stoichiometric films but slow depositions. The surface layer may also increase surface resistivity and the target potential will drop. In order to solve this problem, the gas flow of the reactive gas must be regulated to obtain desired deposition rates and stoichiometry. Figure 7 represents a graph showing the hysteresis loop of the process. The reactive gas flow is increased to obtain desired stoichiometry, though at the critical point the target will become poisoned and the deposition rate will drop instantly.

Figure 7. The hysteresis loop for reactive sputtering. Note that the transition from metal target and compound target takes place at two different gas flows.

Decreasing the gas flow will not instantly exit the system from poisoned state as it takes time for the reactive gas to desorb from the chamber walls. An automated feedback loop can be used to maintain the reactive gas flow in the transition region between poisoned mode and elemental sputtering.

RF sputtering

Another issue regarding sputtering is depositing electrically insulating materials. As the deposition proceeds and target atoms are ejected, secondary electrons will form, leaving behind a positive charge on the target. The accumulation of these charges will disrupt the argon plasma by repelling the positive ions, decreasing secondary electron formation and eventually extinguishing the plasma. Also, in order for the target to work at appreciable currents, very high potentials (10^{12} V) are required which is not practical. In this case, we can use radio frequency magnetron sputtering which utilizes an AC power supply instead of a DC one. The effective resistance of dielectrics can be varied with the frequency of the electric current and reasonable voltages can sustain the electric current by seeing a lower impedance. With the anode and cathode switching signs at a frequency of 13.56 MHz, the charge build up will be neutralized (self-biasing) with the electrons preventing the disruption of the plasma. The heavier ions cannot follow the switching and because the chamber and substrate are very large, they will not be sputtered in negative bias. One should note, however, that these power sources are more complex (and expensive) and because only half the time the target is in negative bias, deposition rates decrease⁷.

3. The microstructural evolution of thin films

The microstructural features of a thin film govern many of the electronic, optical and mechanical properties. These features include uniformity, grain size, texture, thickness, etc. Therefore, there is a need for understanding and control of the microstructural evolution of thin films.

Epitaxial growth

Polycrystalline thin films have multiple applications especially as protective coatings for their desired chemical inertness and/or superior mechanical properties, but electronic and optoelectronic devices require epitaxial thin films. This term was first coined in 1928 by Royer⁸ which is derived from the Greek words *epi* (ἐπί), meaning "above", and *taxis* (τάξις), meaning "an ordered manner". Depositing a thin film on a monocrystalline substrate requires the lattice of the film and substrate to match each other with the least lattice mismatch possible. If coherent heteroepitaxial growth is desired, strain will ultimately be present but a small lattice mismatch can be afforded. The strain will increase with film thickness. By the following equations, one can calculate both the lattice mismatch (ϵ) and critical thickness (d_c) of the film in which the film will be strained but without any major defects:

$$\epsilon = (a_s - a_L)/a_L \quad (\text{eq. 4})$$

$$d_c \approx a_s / (2 |\epsilon|) \quad (\text{eq. 5})$$

where a_s is the lattice parameter of the substrate and a_L is the lattice parameter of the deposited layer.

In the case where the film thickness exceeds the critical limit (which usually is the case), relaxation will occur at the film/substrate interface by the introduction of misfit dislocations. One alternative solution would be to deposit films of a seed layer on the substrate. The seed layer should have a low mismatch with the thin film to insure that the relaxation will be confined to the interface with the substrate.

Thus, the lattice mismatch controls the self-assembly deposition process which is categorized into three different growth mechanisms (figure 8):

The Volmer-Weber process: Surface tension is high, adatom-adatom bonding is preferred, and island growth is distributed across the substrate surface. The high lattice mismatch and surface roughness of such films initially make this growth process undesirable for epitaxial films. However, this process can be very valuable for the synthesis of self-organized zero-dimensional quantum dots used for optoelectronics⁹.

The Frank-van der Merwe process: Adatoms tend to bond with the substrate instead of each other and the stress from lattice mismatch is low, resulting in a layer by layer growth process of smooth films^{10 11 12}.

The Stranski-Krastanov process: When surface tension and lattice mismatch is in between the two previous situations, the film will grow in a layer by layer fashion until reaching the critical thickness. At this point, the reduction of strain energy will result in island growth. A growth process like this will result in polycrystalline films if the film thickness exceeds the critical limit¹³. This growth mode is also used for self-organized quantum dot synthesis.

Figure 8. Thin film self-assembly growth mechanisms. Depending on the extent of the lattice mismatch between the film and the substrate, the film would follow one of the three processes.

Polycrystalline Thin Films

The deposited film will arrange itself in a way to obtain maximum stability and therefore minimum energy. Thus structural evolution is determined by the minimization of the Gibbs free energy:

$$G = G_0 + \sum A_i \gamma_i + \sum G_{sj} \quad (\text{eq. 6})$$

where A_i is the area of the interface, γ_i is the excess free energy of the interface and, G_{sj} is the energy stored in the strain-inducing defects. G_0 is the minimum Gibbs free energy of a perfect bulk crystal which is a constant. $A_i \gamma_i$ represents the excess free energy of a crystallite which stems from grain boundaries (GB), film-substrate interface and film free surface. As a result, the reduction of $\sum A_i \gamma_i$ will determine the outcome of the preferred orientation and grain size. Also, various defects present in the film like impurity atoms, vacancies, dislocations, stacking faults, etc. will induce strain inside the film. In order to minimize $\sum G_{sj}$, the growth process will go towards strain reduction which affects preferred orientation. In cases where the strain propagates into the film structure, film texture as a function of film thickness is seen.

Formation kinetics

The deposition initially starts by the formation of stable nuclei that come from impinging atoms on the substrate surface which consequently leads to stable clusters. The nucleation rate is directly dependent on the deposition rate and substrate temperature. In the case of sputtering, the deposition rate depends on the working gas pressure, the target material sputtering yield, and the energy of the impinging ions. At this point a competition between various factors emerge. Too high substrate temperatures may cause the adatoms to re-evaporate from the substrate while too low temperatures will decrease surface mobility of the adatoms. The ratio of the substrate temperature over the melting temperature of the deposited material (known as the homologous temperature, T_s/T_m) governs surface diffusion and atom mobility. In case of high enough mobility, the atoms tend to nucleate around surface defects and form crystallites with a selected orientation to enhance stability. Low mobility will result in fine grains or amorphous structures with a high degree of shadowing effects. In order to increase mobility without increasing the temperature, a negative substrate bias is a method of choice in sputtering. The incoming argon ions provide sufficient energy for grain boundary migration, coalescence, and layer densification. However, too high energies will result in structural defects inside the film, re-sputtering and ion implantation, and the incorporation of gas pockets.

As the atoms accumulate to form larger and larger nuclei, islands take shape. Each island has its own unique growth rate and preferred orientation which stems from minimizing the Gibbs free energy. When the islands grow large enough, they come into contact (island coalescence). Depending on the diffusivity and mobility of the atoms, these islands may remain separated via grain boundaries or some larger islands grow by absorbing smaller neighboring islands. In low temperature depositions when there is a small contribution from ion irradiation, the grains tend to be small with no GB migration. The resulting films will turn porous and polycrystalline (or even amorphous). The absence of surface diffusion and atom mobility prevents the system to overcome the activation barrier and the resulting structures will remain in a metastable state.

In the case of high surface diffusion and atom mobility, the island coalescence comes to the point in which more energetically favorable islands will grow at the expense of more unstable ones. In this case, GB migration and bulk diffusion have a pronounced effect, and recrystallization occurs. Also, the GB interface energies decrease as grain coarsening decreases the number of grain boundaries. Islands with a denser set of planes are more favored; (111) planes for fcc structures, (110) for bcc, and (0002) for hcp structures¹⁴.

In addition to the film deposition process, post growth annealing of the films can also play a role in altering the microstructure by providing enough energy for additional GB motion and bulk diffusion leading to a textured film composed of large crystallites with smooth surfaces.

After a continuous film is developed, film thickening can proceed in different directions. In case of low mobility situations, incoming atoms will re-nucleate on the previous grains and atomic shadowing will result a fibrous film with a high degree of porosity. A structure like this is also favored when defects and impurities are present, hindering surface diffusion. In the case of suitable surface diffusion and mobility, localized epitaxial growth will insure that arriving atoms will continue the crystallite growth resulting large columnar grains with preferred orientation and smooth surfaces. Deposition rates also play a role in determining the microstructure. Too low deposition rates will result an increase in the impurity inclusion in the film (preventing GB motion, atom mobility and introducing defects) while too high deposition rates will decrease the required time for atoms to position themselves for surface diffusion and

local epitaxy. The atoms will be “buried” under new incoming atoms and the film will turn porous.

At this point, a quantitative standard that will relate the main deposition parameters with the microstructure of the film can be of great importance. Movchan and Demchishin¹⁵ were the first to propose a Structure Zone Model (SZM) guideline which relates microstructural features to the T_s/T_m ratio (substrate temperature over melting temperature, see figure 9). Other prominent growth parameters like gas pressure effects and substrate bias were also taken into account by Thornton^{16 17} and Messier et al.¹⁸ in later Structure Zone Models.

It is shown that at low T_s/T_m , the film will have a fibrous structure, composed of small crystallites or fully amorphous structures. The incoming atoms do not have enough kinetic energy to overcome the activation barrier for atom mobility and surface diffusion. This will result in atomic shadowing, structural defects, and porosity and the film will be known as a “zone I” structure.

In case of increased T_s/T_m or with the help of ion irradiation (in which momentum transport from incoming positive ions to the surface atoms occur), the film will enter the “transition zone”. The adatoms will now have enough energy for surface diffusion and GB motion. Zone T thin films are composed mainly of various crystallites with their respective crystal orientation engaged in competitive growth. Crystal planes with lower free energy will prevail and continue to form thin columnar grains with rough surfaces.

“Zone II” structures form when bulk diffusion is high. At this point liquid like coalescence is seen and grain coarsening occurs with and after island coalescence resulting a highly textured film composed of large columnar grains.

Figure 9. Structure zone models for thin films. As the T_s/T_m ratio increases, enhanced adatom mobility transforms the fibrous and porous film into a dense film composed of large crystal grains. Drawn based on an original from P.B. Barna and M. Adamik¹⁹.

4. Thermoelectrics: basics and challenges

The Seebeck effect, which was discovered in the early 1800s, has promise to address environmental concerns by providing more efficient energy cycles. Internal combustion engines and industrial facilities produce large amounts of waste heat which can be recycled to decrease fuel consumption. This is done by directly transforming a temperature gradient into an electrical current, a process used for deep-space exploration which requires reliable and long-lasting power generators. The opposite of the Seebeck coefficient, the Peltier effect, is used in some consumer applications and has also drawn interest for its prospective role in providing a reliable and compact heat spot cooling method for high tech electronic and optoelectronic devices without the need for a coolant or any moving parts.

Although the proposed applications seem promising, progress in the development of effective thermoelectric devices has been rather slow. This is mainly due to the limitations on their efficiency, expressed through the dimensionless figure of merit zT ²⁰:

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \quad (\text{eq. 7})$$

where $\sigma = 1/\rho$ is the electrical conductivity, α is the Seebeck coefficient, T is the absolute temperature and κ is the thermal conductivity of the material. The product $\alpha^2 \sigma$ is known as the power factor. Note that the quantity “ zT ” is preferred over “ z ”. The reason is that $\frac{\alpha^2 \sigma}{\kappa}$ changes with temperature. Thus there is a need for thermoelectric materials for different temperature regimes. This equation is used to evaluate the performance of a thermoelectric device. If zT reaches infinity, the efficiency of the thermoelectric device will reach the theoretical maximum of a Carnot heat engine, but typically the zT of modern thermoelectric devices are close to unity. Unfortunately, the parameters α , σ and κ , do not change independently under ordinary circumstances because of their interdependence with each other. As a result, the main goal of a materials scientist would be to maximize the power factor of a thermoelectric device and minimize its thermal conductivity.

Basics

If one side of a thermoelectric device is heated and the other side is kept at a fixed low temperature, an electric current can be measured (figure 10, left image).

The opposite is also true: if an electric current is passed through a thermoelectric device, one side will heat up while the other side will start to cool. This is known as the Peltier effect (figure 10, right image).

Figure 10. Schematic illustration of a thermoelectric couple in power generation (left) and solid-state refrigeration (right).

The cause is the thermoelectric effect which occurs when a temperature gradient is established over a conducting or semiconducting material (figure 11). When thermal energy is introduced, the low energy charge carriers migrate from the hot side of the material to the cold side, causing an electric field inside the material.

Figure 11. When a thermal gradient is established, the more energetic charge carriers (electrons and holes) with larger mean free paths migrate towards the cold side of the thermoelectric junction until a stopping electric field is established.

There are a couple of issues that one must take into account regarding thermoelectrics. Although zT gives a good idea of whether a thermoelectric material has the desired potential, other parameters like device efficiency must also be considered. First, thermoelectric devices work with material pairs. Using material with the same charge carrier nature will cancel the current, as a result n-type and p-type semiconductors are used. A more applicable equation regarding semiconductor couples is:

$$zT = \frac{(\alpha_p - \alpha_n)^2 T}{[(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2}]^2} \quad (\text{eq. 8})$$

The p and n indices represent n-type and p-type semiconductors, which will form the thermoelectric couple. Note that metals have high thermal conductivity and very low Seebeck coefficient values and insulators (like glass) have almost no electrical conductivity, thus the power factor and the figure of merit of these materials render them useless for thermoelectric devices unless used in combination with semiconducting material.

If one plans to obtain the efficiency of the device the equation would be:

$$\eta_{TE} = \frac{W}{Q_H} = \frac{T_H - T_C}{T_H} \left(\frac{(1 + zT_M)^{1/2} - 1}{(1 + zT_M)^{1/2} + T_C/T_H} \right) \quad (\text{eq. 9})$$

where T_M is the mean temperature of the device. Based on the above equation and its relation to the Carnot engine efficiency, at operating temperatures between 300 and 800 K and a zT of 3, one can expect efficiencies of above 40% of the Carnot efficiency if such zT values could be achieved.

Typical thermoelectric materials are narrow band-gap semiconductors, for increased electrical conductivity. High electron mobility is also required ($\mu \approx 2,000 \text{ cm}^2 (\text{V} \cdot \text{s})^{-1}$), but the carrier concentration should be comparatively low so that both the electrical conductivity and the Seebeck coefficient can be addressed. The following equation explains the relationship between carrier concentration and the Seebeck coefficient:

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \quad (\text{eq. 10})$$

A concentration between 10^{19} and 10^{20} carriers per cm^3 is considered as an appropriate amount²¹ which is material dependent. The previous equation also shows that the carrier effective mass has a profound effect on the Seebeck coefficient. The m^* refers to the density-of-states effective mass, which increases with a large slope of the density of states at the Fermi surface, increasing the Seebeck coefficient. However, a large effective mass will also decrease electron mobility and consequently, the electrical conductivity. It can be clearly seen that semiconductors with the required thermoelectric properties must be carefully selected, tailored and optimized to reach desired performance.

If the operating temperature of the device is increased, larger band gaps are needed for thermal conductivity control. High temperatures also cause diffusion, chemical reactions and contact impairment which can seriously deteriorate the properties of the device. And as the maximum zT value changes with temperature, no one thermoelectric material can be used for all applications and thermoelectric materials for different temperature ranges are required. Traditionally, bismuth telluride (Bi_2Te_3) for low temperature, lead telluride (PbTe) for mid-temperature and Si/Ge alloys are used for high-temperature regimes.

However, telluride based thermoelectrics are scarce, expensive and have thermal, chemical and mechanical stability issues^{22 23 24}. Si/Ge alloys used for long endurance applications (e.g., the Voyager space program) have excellent stability, but require very high (~ 1000 °C) temperatures fueled by expensive ²³⁸plutonium oxide for optimal usage.

TE property optimization

The main focus on research regarding thermoelectric devices is mainly the development of semiconductor structures with optimum thermoelectric properties. For this to be achieved, one must increase the power factor and decrease the thermal conductivity of each of the semiconductor couples. The challenging aspect is that these two parameters do not change independently. In 1995 Slack²⁵ proposed an idea about what are the characteristics of a good thermoelectric material. He explained that thermoelectric semiconductors must have the electrical conductivity of a crystal and the thermal resistivity of glass. This is now known as the Phonon Glass-Electron Crystal approach (PGEC).

Thermal conductivity stems from charge carrier conduction and lattice vibrations (phonons). Charge carriers are required for high power factors, thus research is mainly focused on minimizing thermal conduction by phonon scattering. The total thermal conductivity is given by the following:

$$\kappa = \kappa_l + \kappa_e \quad (\text{eq. 11})$$

κ_e is the electronic contribution of thermal conductivity, and is naturally tied to the electrical conductivity by the Wiedemann-Franz law:

$$\kappa_e = L_0 \sigma T \quad (\text{eq. 12})$$

in which L_0 is the Lorentz number. This relationship and its dependence on the electrical conductivity σ shows that not much can be done to decrease the electronic contribution of thermal conductivity as the power factor will also decrease.

On the other hand, κ_l is:

$$\kappa_l = \frac{1}{3} (v_S C_V L_{ph}) \quad (\text{eq. 13})$$

in which v_s is the speed of sound, C_V is the heat capacity at a constant volume and L_{ph} is the mean free path of the phonons. At room temperature, v_s and C_V are independent of material type, so the main focus would be on the mean free path of the phonons and methods to decrease it to the point that it is essentially equal to the interatomic spacing of the constituent atoms. One such method would be alloying. This would cause short wavelength acoustic phonon scattering by introducing atomic sized point defects. An example would be the Si/Ge alloy used for high temperature radio isotope thermoelectric generators used by NASA. Both of these materials have a high thermal conductivity but alloying results enhanced phonon-phonon and phonon-electron scattering²⁶.

Complex inorganic crystals that include heavy metallic atoms also cause phonon scattering. If voids are created in the lattice structure which are partially or completely filled with heavy atoms, an effect known as rattling occurs which can also scatter phonons²⁷. These techniques are used to reduce the thermal conductivity below the alloy limit²⁸ by scattering mid to long wavelength phonons. Quantum dots dispersed in a solid matrix can be formed in a variety of ways, including phase separation of an alloy during bulk crystal growth or by the Stranski-Krastanov or Volmer-Weber mechanisms during epitaxial growth. Research has shown that ErAs nanodots in an InGaAs/InGaAlAs matrix²⁹ will cause effective scattering with the scattering cross section being proportional to b^6/λ^4 , where b is the size of the nanodot and λ is the acoustic phonon wavelength (figure 12). When these rattlers and quantum dots are unevenly distributed or when the size varies, the scattering effects increase by reacting with a larger phonon spectra.

Figure 12. Schematic illustration of various phonon scattering mechanisms in action.

Another use of nanotechnology in the development of thermoelectric devices is the synthesis of superlattices to create charged-carrier confinement, phonon localization, specular scattering of phonons at interfaces due to acoustic mismatch and scattering of phonons at defects (dislocations from lattice mismatch)^{30 31 32}. It has been shown that superlattice thin films with various/random thicknesses increase the scattering of phonons at the film interface. Cahill et al. presented multilayers that have a thermal conductivity comparable with air³³ (approximately $0.03 \text{ Wm}^{-1}\text{K}^{-1}$). Nanocrystals, polycrystalline structures and highly disordered thin film crystal layers are also known to decrease the thermal conductivity. Such procedures will result in a limited flow of hot electrons which will reduce electrical conductivity, but at high enough operating temperatures, it will mostly affect the thermal conductivity of the thermoelectric device and as a result, enhance zT .

Most modern approaches into maximizing zT have been done by decreasing the lattice contribution of thermal conductivity. It seems that this specific approach does work well in improving current thermoelectric materials. However, researching unexpected material is an avenue to be explored. Semiconducting hard coatings like scandium nitride (ScN) or chromium nitride (CrN) show good thermal, chemical and mechanical properties at high temperatures. ScN is known to have high power factors³⁴ (max: $3.3 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at 800 K) and CrN is known to have a Seebeck coefficient close to $-230 \text{ } \mu\text{V/K}$ (discussed in paper I) and a thermal conductivity^{35 36} between 2 and $4 \text{ Wm}^{-1}\text{K}^{-1}$. On the negative side, ScN has a relatively high thermal conductivity³⁷ ($8.3 \text{ Wm}^{-1}\text{K}^{-1}$), while as CrN has a low electrical conductivity of approximately $10 \text{ m}\Omega\text{cm}$ prompting additional research. As ScN and CrN are abundant compared to traditional thermoelectric materials, they can be proposed for synthesis based on the PGEC method for thermoelectric research.

5. Theoretical calculations: phase stability and structure prediction

Modern theoretical methodologies and high speed computers allow researchers to study and predict the physical and chemical properties of solids directly from the fundamental equations of quantum mechanics and thermodynamics³⁸. Experimental research in material science is time consuming and expensive, thus theoretical calculations can be used to guide experimentalists and prevent redundant work.

The Schrödinger equation

Quantum mechanics provides a theoretical description of the microscopic world. As most states of matter are composed of positively charged nuclei surrounded by negatively charged electrons, quantum mechanics is needed and in principle capable of explaining all material properties. Thus, the Schrödinger equation is considered a great achievement in physics:

$$\hat{H}\Psi = i\hbar \partial\Psi/\partial t \quad (\text{eq. 14})$$

$$\Psi = \Psi (r_1, r_2, r_3, \dots, R_1, R_2, R_3, \dots, t) \quad (\text{eq. 15})$$

$$H = -\frac{1}{2} \sum_{i=1}^n \frac{\hbar^2}{m_e} \nabla_i^2 - \frac{1}{2} \sum_{I=1}^n \frac{\hbar^2}{M_I} \nabla_I^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (\text{eq. 16})$$

where equation 14 is the time-dependent Schrödinger equation, equation 15 is the wave function of the quantum system, consisting of r_i (the coordinates of the i^{th} electron), R_I (the coordinates of the I^{th} nucleus) and t (time). Equation 16 is the Hamiltonian operator. It is needed to describe the energy state of the wave function and consists of five separate terms: the kinetic energy of electrons, the kinetic energy of the nuclei, electron-nucleus attraction, electron-electron repulsion, and nucleus-nucleus repulsion. It was this equation and other advances in quantum mechanics that prompted Dirac to announce in 1929 that: “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of

chemistry are thus completely known, ...”, but in real macroscopic materials, n_i and N_i are close to 10^{23} particles, which makes it necessary for us to simplify the equation otherwise “... the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”³⁹.

An approximation used to simplify the problem is the Born-Oppenheimer approximation, where the motion of the electrons and the nuclei are separated when solving for the electronic degrees of freedom. Second, we have the Bloch theorem, which states that due to the periodicity of the crystal lattice, all wave functions must have the same periodicity of the lattice, making it sufficient to only solve the electronic problem for one unit cell, and then apply periodic boundary conditions. Although both modifications greatly simplify the problem at hand, a typical unit cell may have a hundred electrons which still renders the Schrödinger equation unsolvable. This is where the electronic density becomes useful.

Density Functional Theory (DFT)

Hohenberg and Kohn⁴⁰ proposed two theorems fundamental to the density functional theory:

Theorem 1: For any system with interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is uniquely determined by the ground state particle density $n_0(\mathbf{r})$ up to an additive constant.

Theorem 2: A universal functional for the energy $E[n, V_{\text{ext}}]$ in terms of the density can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. $E_0 = E[n_0]$ is the global energy minima for any particular potential.

In general, instead of determining the allowed energy states by solving the many-body wave function dependent on $3N$ coordinates (N being the number of electrons), an electronic density which only depends on 3 coordinates and uniquely defines the ground state properties of the equivalent many-body system can be used. Any many-body system with an external potential can be defined by a universal functional of energy.

Minimizing this functional will lead to the global energy minimum and consequently, the ground state properties of the many-body system.

These theorems have the disadvantage that they do not introduce any universal functional needed to calculate the ground state properties. However, Kohn and Sham⁴¹ proposed a method in which the many-body electrons is simulated by a fictitious system of non-interacting particles. The fictitious system is constructed such that the energy of these Kohn-Sham (KS) particles is minimized by the same density which minimize the energy of the real electronic system. The Kohn-Sham particle system is described by:

$$H_{eff}\psi_i(r) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{KS}(r) \right] \psi_i(r) = \epsilon_i\psi_i(r) \quad (\text{eq. 17})$$

where $\hbar$ is the Plank constant, m_e is the mass of an electron, $\psi_i(r)$ is the KS orbitals, ϵ_i is the KS orbital energy and V_{KS} is defined by the Kohn-Sham approach to the density functional theory:

$$V_{KS}(r) = V_{ext}(r) + \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(r)} \quad (\text{eq. 18})$$

which consists of the electron-nuclei interaction, the internal energy of a classical repulsive gas, and the electronic quantum effects (the exchange-correlation term) which stems from non-classical electron repulsion and the many-body contribution to the kinetic energy. In this equation, $n(r)$ is a set of N Schrödinger like KS equations and ψ_i are the KS orbitals:

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2 \quad (\text{eq. 19})$$

Thus, we can simulate real material systems based on the fictitious KS system and the KS total energy functional:

$$E[n] = T[n] + \int V_{ext}(r)n(r) dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{II} + E_{xc}[n] \quad (\text{eq. 20})$$

where $T[n]$ is defined as the independent particle kinetic energy and E_{II} is defined as the interaction between the nuclei. The second term is the energy from the nuclei or any other external potential and the third term is the energy of the classical repulsive gas (Hartree term). These results will allow the calculation of the electronic band structure and phase stability of any hypothetical crystal.

Phase stability

A group of atoms can be organized in a crystal structure, thus determining the electronic properties. However, for a given set of atoms not all crystal structures are stable. A material system is in thermodynamic equilibrium when under the conditions of a fixed temperature, pressure and number of particles, the Gibbs free energy of the material system is at a minimum:

$$G = H - TS \quad (\text{eq. 21})$$

where H is the formation enthalpy, T is the absolute temperature and S is the entropy.

The enthalpy H is given by

$$H = E + PV \quad (\text{eq. 22})$$

E being the total energy of the system, P the system pressure and V the system volume. According to the Gibbs free energy equation, the system is stable when G is at a minimum. In the case of an hypothetical binary alloy composed of element A and element B ,

$$\Delta G_{mix}(x) = G(x) - (xG_A + (1 - x)G_B) \quad (\text{eq. 23})$$

where $G(x)$ is the free energy of the compound, and G_A and G_B are the free energy of elements A and B and x being the A element mass percentage. Therefore the alloy would be stable compared to the elements if $\Delta G_{mix}(x) < 0$ otherwise it will decompose.

$\Delta G_{mix}(x)$ can also be expressed by the mixing enthalpy ΔH_{mix} , and mixing entropy ΔS_{mix} to produce:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (\text{eq. 24})$$

Figure 13 shows the Gibbs free energy for a hypothetical system consisting of phase α and phase β , both with a fixed and equal composition. Phase α is shown to have a lower Gibbs free energy compared to phase β , therefore it is more stable. However, phase transformation requires the system to overcome the potential barrier U , causing phase β to remain in a metastable state. Please note that a lower Gibbs free energy will promote the system to spontaneously undergo transformation, but has nothing to say on the required time and transformation rates for the process⁴² which is studied in chemical kinetics. One well-known example is graphite and

diamond, which are both pure carbon. Graphite has a lower Gibbs free energy compared to diamond and therefore is stable while as the diamond structure is metastable. However, under standard pressure and temperature conditions and in practice, “*diamonds are forever*” as the potential barrier preventing diamond phase transformation to graphite is very large and requires time many orders of magnitude longer than the age of the universe.

Figure 13. Hypothetical Gibbs free energy for an atomic arrangement in the form of phase α and phase β . Phase α has a lower Gibbs free energy and is located at the global minimum of the system compared to phase β which is located at a local minimum, therefore phase α is stable compared to the metastable phase β .

As mentioned previously, DFT calculations are typically performed at a 0 K temperature. The omitted temperature dependence can affect the Gibbs free energy, especially for the case of magnetic material, and may change non-stable phases into stable ones. One good example is chromium nitride which has an anti-ferromagnetic, orthorhombic structure below 280 K and transforms into a paramagnetic, face-centered cubic structure at room temperature⁴³. Also, vibrational energies which are temperature activated can play a decisive role. However, including temperature is considered a challenge in first-principle calculations, which requires powerful computational resources and advanced methods such as the Monte Carlo technique. Nevertheless, for the case of mixing energies and formation enthalpies, such effects are often small for the right set of material. For example, non-magnetic transition metal nitrides which have very high melting temperatures are decent cases where time consuming temperature-

dependent calculations can be avoided in a first round of investigation^{44 45}. Thus, for phase stability calculations the Gibbs free energy global minimum used to determine thermodynamic equilibrium mostly depends on the formation enthalpy of the system:

$$G = H = E + PV \quad (\text{eq. 25})$$

Under normal conditions the pressure (P) is almost zero. In a solid, the internal energy E is composed of a potential energy which originates from atomic interaction and bonding and will be used for constructing an enthalpy diagram.

Figure 14 shows a hypothetical binary enthalpy diagram. It is seen that the formation energy for the compounds are compared to their elemental form. The lowest energy points are connected to each other by the “convex hull”, which is defined as a line that encircles all data points without having any concavities.

To calculate the formation enthalpy per atom (H_{atom}) the following equation is used:

$$H_{atom} = [E_{tot} - n_A(E_{min}^A) - n_B(E_{min}^B)] / n_{A+B} \quad (\text{eq. 26})$$

where E_{tot} is the total energy of the compound phase unit cell, E_{min} is the minimum energy of element A or B and n is the total number of atoms of element A or B in the unit cell. If H_{atom} for any given compound is negative and located on the convex hull, it will be stable, while the remaining data points located above the hull represent metastable or unstable compounds.

Figure 14. Hypothetical enthalpy diagram of elements A and B. The compound mixture in the form of A_2B and AB_2 are located on the convex hull and are stable. However the AB stoichiometry is not located on the hull and is either metastable or unstable.

Simulating equivalent ternaries for scandium nitride

The aim of conducting theoretical predictions in this thesis is to search for a possible, as yet hypothetical, replacement for scandium nitride. ScN is a cubic semiconducting hard coating which has gained interest for thermoelectrics. It has an approximate power factor of $\sim 3000 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 500 °C which is very high for a transition metal nitride⁴⁶. In addition to the power factor, the thermal conductivity of ScN is also high (close to $\sim 10 \text{ Wm}^{-1}\text{K}^{-1}$) resulting a low zT value and consequently, low thermoelectric efficiency. While scandium is a reasonably abundant element⁴⁷, it is expensive due to modest demand which limits world production. Also, scandium is an isotopically pure element, which means that phonon scattering due to isotope impurities is absent.

In a paper published in 2014 by Alling⁴⁸, it was proposed that one could search for an equivalent ternary based on ScN. The ternary would have a similar electronic band structure and Seebeck coefficient, while as the substituted elements would be better at phonon scattering. An example would be a naturally layered crystal structure. In his paper, TiMgN_2 was chosen, based on the fact that magnesium and titanium belong to the groups before (group 2) and after (group 4) scandium in the periodic table. The results of the research show that not only TiMgN_2 is predicted to be stable,

but it is also a semiconductor with a 1.1 eV band gap which crystalizes into the NaCrS_2 superstructure (figure 15). This structure can also be described as a NaCl (B1) based superstructure which includes three alternating layers of titanium and magnesium. These results open the opportunity to study other replacements for scandium such as zirconium and hafnium, as both of these elements are heavier than scandium and titanium. They also consist of multiple stable isotopes which may enhance phonon scattering. This is discussed in paper II.

Figure 15. TiMgN_2 crystalized into the trigonal NaCrS_2 superstructure. Note the alternating layers of titanium and magnesium compared to the smaller nitrogen atoms.

6. Concluding remarks and future work

The results from paper (I) concludes that epitaxial cubic CrN thin films show good thermoelectric properties with a high power factor close to $5000 \mu\text{Wm}^{-1}\text{K}^{-2}$ at room temperature. The results show that the synthesis process is sensitive to the gas flow ratio as increasing the nitrogen content of the gas flow will introduce multiple grain boundaries. This in turn increases electrical resistivity. On the other hand, decreasing the nitrogen content will result in the formation of a secondary phase of chromium nitride: hexagonal Cr_2N . Small amounts of Cr_2N form in the shape of randomly dispersed nano-inclusions inside a CrN matrix. The same can also be said for deposition temperature, as too low deposition temperatures increase film surface roughness and grain boundaries by limiting surface diffusion and coalescence while as too high temperatures will cause total phase transformation from cubic CrN to hexagonal Cr_2N . These studies led to the conclusion that the best thermoelectric properties belong to the phase pure and single crystal CrN films.

Although the results from paper (I) are promising, the figure of merit for single crystal CrN thin films is estimated to be 0.5 based on published thermal conductivity measurements. Chromium is relatively cheap and abundant, and chromium nitride in comparison with many benchmark thermoelectric material has superior mechanical, chemical and thermal stability, but the figure of merit is medium to low. One proposal to enhance thermoelectric zT , is to decrease the electric resistivity by doping and alloying. Elements such as vanadium, tantalum, hafnium and tungsten could prove suitable as all three form conducting nitrides. Rock-salt cubic vanadium nitride (VN) has a very similar lattice parameter⁴⁹ to CrN (approximately $4.13 \text{ \AA}$), making it possible to alloy CrN without disrupting the single crystal nature of the film. In addition, the synthesis of $\text{CrN}/(\text{Cr}, \text{V})\text{N}$ superlattices is being studied as a means to reduce thermal conductivity by introducing quasi-random layer thickness in order to enhance interface phonon scattering. Rock-salt cubic hafnium nitride (HfN) could also prove as a suitable candidate when considering the relative atomic mass⁵⁰ of hafnium compared to chromium (178.49 vs 51.99). The relatively heavy elements tantalum and tungsten could potentially form either hexagonal nanoinclusions (Ta_2N and W_2N) or accept the rock-salt cubic structure. In any case, the effects of adding such elements to CrN could alter the

electrical resistivity, thermal conductivity and the Seebeck coefficient value.

Future research would also require thermal conductivity measurements. Although the Cr_2N nanoinclusions did not show any improvement in the power factor, studying the effects of these nanoinclusions on the thermal conductivity is also needed.

In addition to the experimental research, the theoretical studies from paper (II) showed that TiMgN_2 , ZrMgN_2 and HfMgN_2 which were modeled over cubic scandium nitride all predict stable crystal structures for the given stoichiometries. These results predict that it is possible to synthesize all three compounds and to influence the crystal structure by choosing different substrates as trigonal NaCrS_2 and monoclinic LiUN_2 both show tendency for stable crystal structure formation. The band structure calculations also predicts semiconducting properties which may have prospective thermoelectric properties better than that of ScN .

Thus, actual laboratory synthesis is needed to determine if TiMgN_2 , ZrMgN_2 and HfMgN_2 exist. Synthesizing these ternaries in either the trigonal NaCrS_2 or the monoclinic LiUN_2 structures could be possible by methods such as DC reactive magnetron sputtering which deposit compounds far from thermodynamic equilibrium. Actual synthesis would require a UHV chamber, suitable substrates according to their crystal structure and lattice parameter (e.g., hexagonal GaN , hexagonal SiC ...) and the required elemental targets (Mg , Ti , Zr , and Hf). The synthesis of these ternaries could lead to power factors similar or better than ScN but with lower thermal conductivities.

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List of included papers

Microstructure and Thermoelectric Properties of Chromium Nitride Thin Films

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Manuscript in final preparation

Theoretical Studies on MeMgN₂ Superstructures (Me = Ti, Zr, Hf)

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