CHARACTERIZATION OF THE THERMAL ELECTRON EMISSION PROPERTIES OF BORON-DOPED POLYCRYSTALLINE DIAMOND FILMS FOR USE IN ENERGY CONVERSION

By

William Francis Paxton IV

Thesis

Submitted to the Faculty of the

Graduate School of Vanderbilt University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

in

Electrical Engineering

May, 2011

Nashville, Tennessee

Approved:

Professor W. P. Kang

Professor J. L. Davidson

To my wife, Megan

ACKNOWLEDGEMENTS

I would first like to thank my advisor, Dr. Jim Davidson, who gave me my first experience as a researcher during my senior year as an undergraduate. Since then, Dr. Davidson has exceeded the role of a typical academic advisor through his guidance and mentorship not only in graduate school but also in life experiences. I am also extremely thankful for Dr. W. P. Kang, who has been a strong asset in his knowledge and support of my research objectives. Additionally, I would like to thank Mick Howell, without whose keen insight on practical research methods, this project could never have been performed.

In conclusion, I would like to thank my wife Megan, my parents Bill and Lucy, and my sister Crissy who have always pushed me to do my best.

TABLE OF CONTENTS

ABSTRACT

Thermionic energy conversion is a relatively unexplored technology for the efficient conversion of thermal energy directly to electrical energy. In a thermionic converter, thermally excited electrons are emitted from the surface of a material (defined as thermionic emission) which are then used to drive a load. Emission current density increases exponentially with the temperature of the electron emitter leading to a highly efficient conversion device at elevated temperatures. In this study, the thermionic emission properties of boron-doped polycrystalline diamond are examined for use in thermionic energy conversion.

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

The research addressed herein presents a method for characterizing diamond films for use in the direct conversion of thermal energy to electrical energy by means of thermionic emission. Diamond material properties and current applications are covered in this chapter. Electron emission mechanisms and their relation to diamond are also explored.

1.1 Diamond as an electronic material

Diamond has long been appreciated for its optical and mechanical properties but recent research has begun to explore diamond's electrical properties. Diamond is a unique material that takes the same lattice structure as silicon where each carbon atom is covalently bonded to its four nearest neighbors.

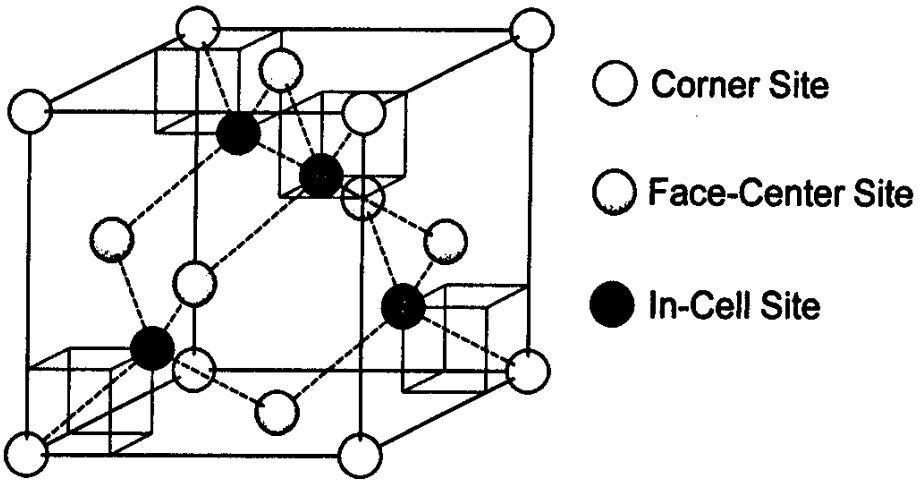

Figure 1.1 Image of the diamond lattice [1]

As with silicon, diamond has the ability to act as a semiconductor when one of these carbon atoms is replaced with a dopant atom such as boron[3]. The semiconductor nature of diamond is extremely favorable to thermionic emission applications and will be discussed in depth later in this study. In order to understand the topics discussed in this research, several physical values must first be defined which can be seen in the semiconductor band diagram in Figure 1.2. The materials bandgap, Eg, is the energy difference between the conduction and valence band; the electron affinity, *x*, is the energy difference between the vacuum level and the conduction band; and ϕ is the work function of the material and can be measured as the difference between the Fermi level and the vacuum level. By examining figure 1.2, it can easily be seen that the work function can be calculated as the distance from the Fermi level to the conduction band plus the electron affinity.

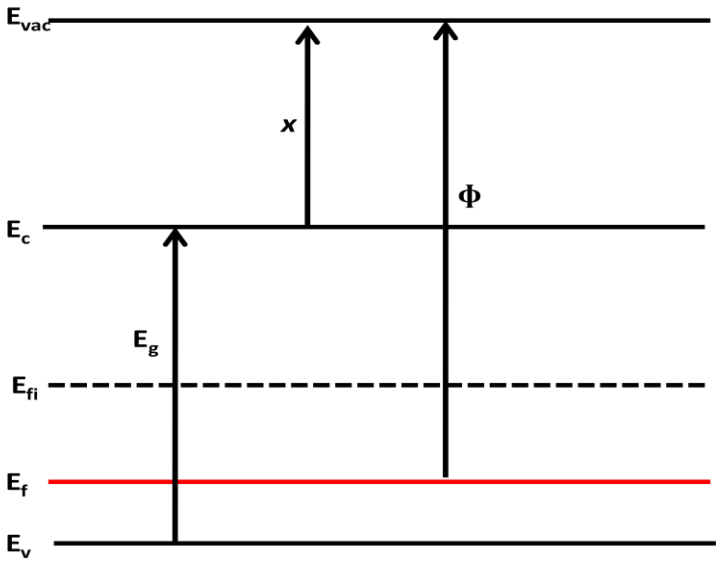

Figure 1.2 Band diagram of a generic p-type semiconductor not drawn to scale where: E_{vac} the vacuum level; E_c the conduction band energy; E_{fi} the intrinsic Fermi level (approximately halfway between E_c and E_v); E_f the Fermi level with a p-type dopant; E_v the valence band; and E_g, *x*, and ϕ defined as the band gap, electron affinity, and work function respectively.

The position of the Fermi level in Figure 1.2 is a function of the dopant concentration and dopant type and can be positioned between E_c and E_v. For an n-type dopant such as phosphorus, the Fermi level will be positioned above E_i. The Fermi level is the energy level at which electrons have a 50% probability of occupying. In an ideal semiconductor, no states can exist between the conduction and valence band so the Fermi level can be thought of as simply the average energy of electrons. This leads to a simple description of work function as the average energy required to remove an electron from a material. The large 5.45eV band gap of diamond[1] (compared to 1.1eV for silicon) allows for a large range of energy levels for the Fermi level. Diamond has also been shown to have an extremely low to negative electron affinity[4] which coupled with the large bandgap allows large variations of work functions to be achieved by simply changing the dopant concentration or dopant type.

1.2 Electron emission mechanisms

Electron emission is a transport mechanism that is used in numerous applications such as rectifying vacuum diodes, electron microscopy, and magnetrons to name a few. This mechanism can be separated into three main classes: Thermionic emission, Schottky emission, and Fowler-Nordheim emission with regimes existing between[5]. The first two can be described classically and arise from a heated cathode while the third is a quantum mechanical effect that is independent of temperature resulting from extremely high electric fields (>5V/μm). The classical model requires that electrons must have energy equal to or greater than the material's work function in order to be emitted into the vacuum. Schottky emission differs from Thermionic

emission in that an electric field is used to reduce the effective barrier for electrons to be emitted whereas thermionic emission is solely based on the cathode temperature. The Fower-Nordheim model describes the band bending that arises from high electric fields which electrons can then tunnel through to be emitted into the vacuum.

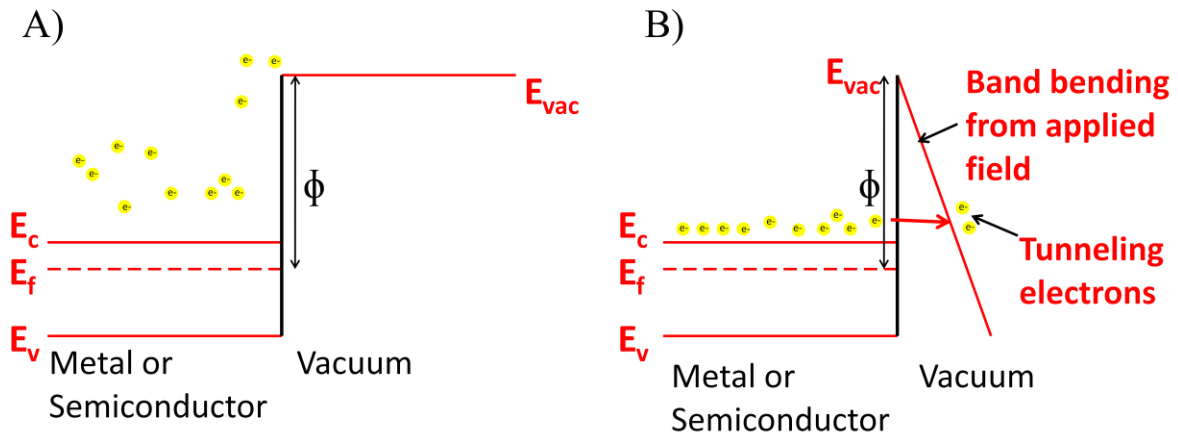

Figure 1.3 A) Classical model of electron emission described by Schottky and Thermionic emission **B)** Quantum mechanical model of electron emission by which electrons are able to tunnel through to the vacuum level due to the band bending from high electric fields.

Current studies in the Vanderbilt University Diamond Lab are examining the electron emission of diamond structures through Fowler-Nordheim Tunneling. By fabricating structures with sharp tips (such as a pyramid) the total effective field required for electrons to tunnel to the vacuum level is decreased due to the field enhancement effect of these tips. Current applications explored for these devices are high frequency vacuum diodes and triodes with transistor-like behavior [6-9].

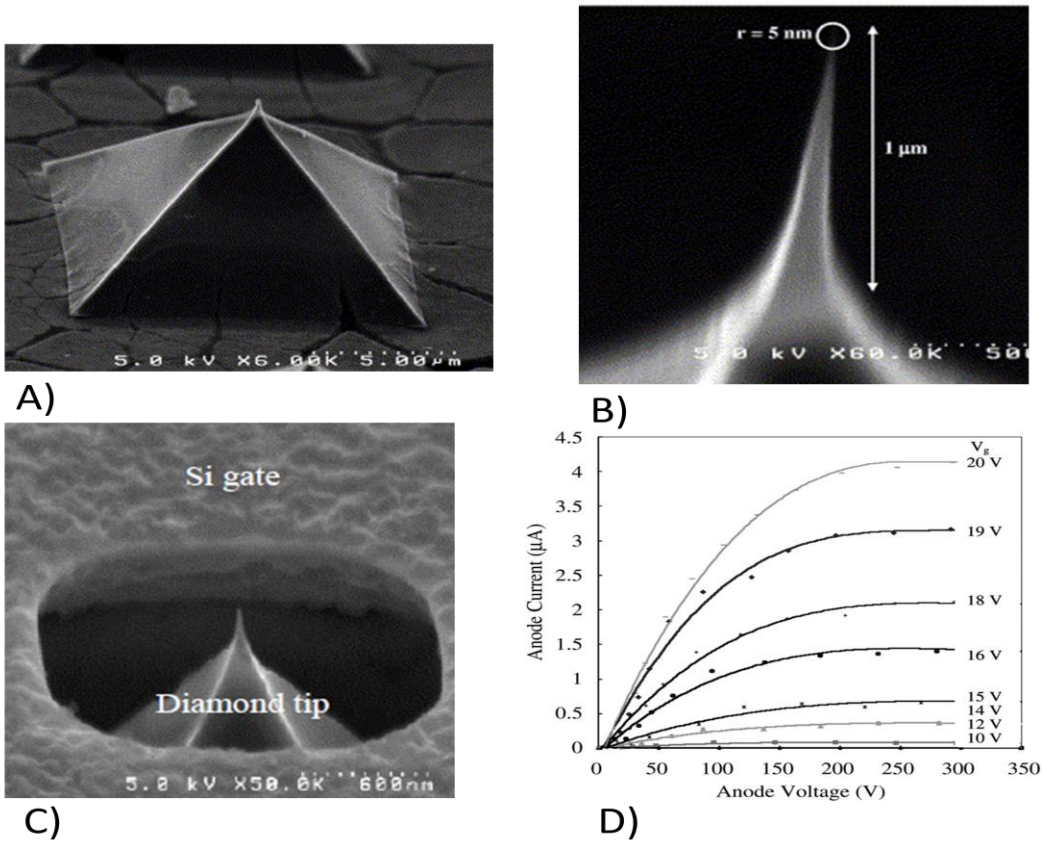

Figure 1.4 A) Micropatterned pyramid for use as an electron emitter. **B)** Sharp tips at the top of the field emitter to promote Fowler-Nordeheim Tunneling at low Electric Fields. **C)** Micropatterned pyramidal electron emitter fabricated with a silicon gate electrode used to extract electrons. **D)** Transistor like behavior of pyramidal electron emitters with a gate electrode.

The following research discussed in this project deals with thermionic emission as a potential method for energy conversion.

CHAPTER II

THERMAL ENERGY CONVERSION BACKGROUND

The impetus for exploring the thermal electron emission properties of diamond films is based fundamentally in direct thermal to electrical power generation. This chapter introduces current power generation methods and the need for new methods to sustain our future growth in energy demands. Thermionic emission and its potential uses in energy conversion are explained. Finally, a detailed analysis of the output characteristics of an ideal thermionic converter is explored.

2.1 Current problems in power generation

Over the past century, the world's demand for electrical energy has been increasing rapidly and is projected to continue to rise significantly in the foreseeable future[10]. Despite this increasing demand, methods used to generate electrical power have remained relatively unchanged. Further, the growing scarcity of fossil fuels illustrates the urgency to utilize renewable energy sources. The current advancements in the fields of material science, physics, and engineering are making new and potentially more efficient methods for power generation possible. This research discusses a recently unexplored method for directly converting thermal energy into electrical energy by utilizing thermionic energy conversion from diamond films.

There are currently numerous methods in existence for the generation of electrical power but few are applicable to meeting the world's increasing large-scale energy demands. The current predominate methods involve a complex multistep conversion of thermal into electrical energy

which begins with acquiring a heat source. In the vast majority of plants this thermal heat source comes from either the burning of fossil fuels or a controlled nuclear reaction. This thermal energy is then converted into mechanical energy by a multiphase working fluid. Lastly, this mechanical energy is converted into electrical energy through large turbines. This multistep process results in high energy loss which consequently leads to relatively low operational efficiencies. The sheer size and complexity of these mechanical generators result in high capital investments and, due to the effects of wear and corrosion that arise from moving parts, demand substantial continuing maintenance.

The need for improved power generation is not limited to large scale distribution. With the recent growth in portable electronics, the call for new compact power generation methods is evident. As these portable electronics become more advanced, so does the power consumption and many of these devices must have decreased performance to reduce these power requirements. Current power sources, such as liquid fuels and radioactive elements, possess high energy density but require a means of converting thermal power to electrical form. Thermoelectric devices are one solution which has proven a reliable method for converting thermal energy to electrical energy without suffering the energy loss from moving parts. Unfortunately, these devices have proven impractical for most applications aside from the most extreme environments (e.g. space travel) due to material limitations and the high temperature gradients required to produce a usable voltage.

Thermionic emission energy conversion offers the possibility of improved power densities and high thermal efficiency as compared to competing approaches. However, thermionic emission has not recently been considered in detail as a mechanism for power generation. In addition, thermionic converters can be powered by virtually any heat source which

does not corrode the materials in the device. By utilizing the radiation tolerant material diamond[11], nuclear heat sources can be used. This effort will produce new knowledge of the theoretical and practical limitations of direct thermal-to-electrical power generation by thermionic emission.

2.2 Thermionic emission

Thermionic electron emission has long been understood (since O.W. Richardson first quantified its behavior in 1903) which describes the influence of temperature on the electron interaction between two mediums[12]. As thermal energy is imparted on electrons in one material (referred to as the cathode), we can predict by Fermi-Dirac statistics that some of these higher energy electrons will have enough energy to be emitted from the cathode into another material (the anode) through direct contact or into vacuum. For the purpose of this research, we are examining the thermal emission of electrons from diamond cathodes into a vacuum.

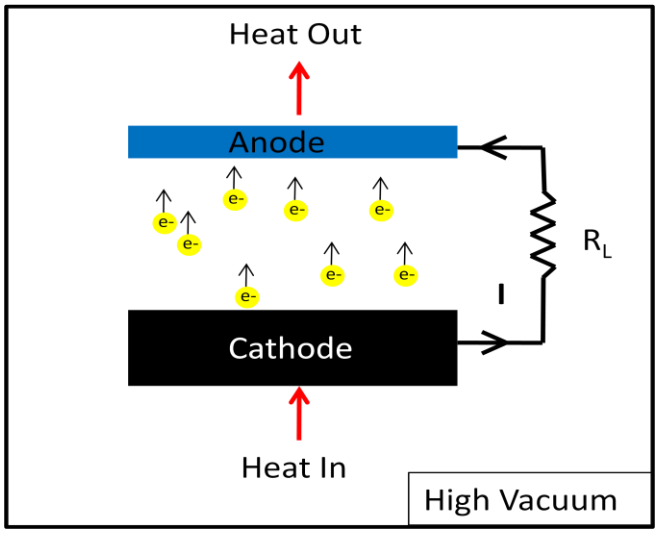

Figure 2.1 Basic design of a thermionic power converter

The idea of utilizing this phenomenon for energy conversion is not original. During the mid 20th century much research went into thermionic energy converters as an efficient means to convert thermal energy into electrical energy with limited success. Previous devices have produced output currents of 20 A/cm^2 at an output potential of between 0.5V to 1.5V and have operated continuously for 5 or more years without failure. Unfortunately these devices were plagued with relatively low operation efficiencies (~20%) due to material limitations which led many researcher to abandon thermionic converters in favor of newer conversion techniques[13].

The fundamental electrode property governing the performance of thermionic converters is the magnitude of the material's work function. This material characteristic can be illustrated as the potential barrier that electrons must overcome to be emitted into a vacuum. The Richardson equation describes the relation between emission current density and emitter work function as follows[12]:

$$J = AT^2 e^{-\Phi/kT} \tag{2.1}$$

where J: Thermionic emission current density (A/cm^2); A: Richardson constant (material specific) (A/T^{2}cm^2); T: Temperature (K); Φ: Material's work function (eV); and k: Boltzmann constant (eV/T).

From the thermionic emission equation at a fixed built-in potential between the cathode and anode, it is observed that emission current density, output power (defined as current multiplied by the built-in potential between cathode and anode), and subsequently the operational efficiency all increase exponentially with the cathode's temperature. It can also be seen that a material with a lower work function can achieve higher current densities at lower temperatures than a material with a higher work function, which implies lower work function values translate into better energy converters. The thermionic converters previously discussed

utilized metallic electrodes with work functions between 3.5eV and 5eV. While lower work functions have been reported for electrodes, they exploit the highly radioactive and toxic element cesium which prevented widespread common usage.

Previous studies at other research institutions have confirmed diamond and diamond-like structures as an ideal candidate for thermionic energy converters. Polycrystalline nanodiamond films grown via Microwave Plasma-enhanced Chemical Vapor Deposition (MPCVD) have demonstrated work functions of 1.4eV[14] with some reporting values as low as 0.9eV[15]. Theoretical calculations demonstrate that this extremely low barrier for electrons to be emitted from a cathode allows for an inherently efficient converter.

It is the purpose of this research project to design a method for characterizing materials for use in a thermionic energy converter. This method must have the ability to accurately quantify the material's electron emission parameters (i.e. the work function and the Richardson constant) in order to determine the optimal configuration for a thermionic converter. Currently at Vanderbilt University, we have the capability to produce two distinct types of diamond, boron-doped and nitrogen incorporated. Boron, unlike nitrogen, has been widely accepted as a substitutional dopant atom in the diamond lattice structure[3]. Much debate still persists on the actual role nitrogen places in diamond. It is because of these reasons, boron-doped diamond films will be the primary film examined in this study.

2.3 Output characteristics of a thermionic converter

Calculating output performance characteristics of a thermionic power converter requires several factors to be considered. A cathode-anode configuration must be constructed where the collector anode has a lower work function value than the cathode in order to provide an

electromotive force to drive electrons across the vacuum gap. As electrons are emitted from the surface of the cathode, a space charge effect arises from the large current densities of negatively charged electrons with little voltage to accelerate them through the gap. This space charge results in an effective barrier for electrons to be emitted which is slightly larger than the materials work function. The inevitable voltage drop arising from electrical connections must also be taken into account. A potential diagram of these factors can be seen in Figure 2.2[2].

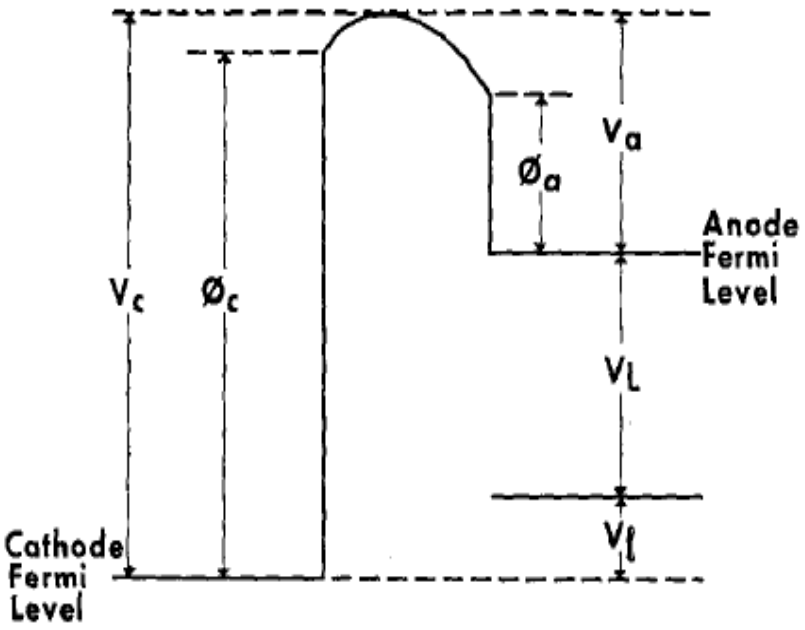

Figure 2.2 Potential diagram for a real world thermionic converter. ϕ_c and ϕ_a are the work functions of the cathode and anode respectively; V_c and V_a are the potential differences between the top of the potential barrier in the interelectrode space from the Fermi level of the cathode and anode respectively; V_L is the potential drop across an external load; and V_l is the potential drop from the necessary electrical connections[2].

By examining the potential diagram in Figure 5.1, it can be seen that the Richardson equation must be modified to account for the larger potential barrier V_c rather than the materials work function leading to the equation:

$$J_C = A_C T_C^2 e^{-V_c/kT_C} \quad (2.2)$$

where J_C: Cathode thermionic emission current density (A/cm^2); A_C: Cathode Richardson Constant; T_C: Cathode temperature; and V_C: Effective potential barrier for electrons to overcome in order to be emitted into the vacuum. Because the Richardson equation pertains to all materials, reverse electron emission current arising from the anode must be accounted for in a similar manor as:

$$J_A = A_A T_A^2 e^{-V_A/kT_A} \quad (2.2)$$

where J_A: Anode thermionic emission current density (A/cm^2); A_A: Anode Richardson Constant; T_A: Anode temperature; and V_A: Effective potential barrier for electrons to overcome in order to be emitted into the vacuum from the anode. Assuming that 100% of the electron emitted are collected, we can recognize a net total current as $J_T=J_C-J_A$.

$$J_T = A_C T_C^2 e^{-V_c/kT_C} - A_A T_A^2 e^{-V_A/kT_A} \quad (2.3)$$

By neglecting the potential drop arising from electrical connections we can realize the output power density of an ideal thermionic converter. The net potential, V, arising in this ideal converter can be described as the difference between the effective cathode and anode barriers for electrons to be emitted into a vacuum with $V= V_c-V_a$.

The energy conversion efficiency can be calculated by dividing the power density produced by a thermionic converter by the total heat input rate per unit area[16]. The power

density produced by the system is simply the total emission current density multiplied by the net potential. The input heat rate per unit area, q_E, is a function of the heat removed by electron emission, q_e; the heat removed by thermal radiation, q_r; and the heat conducted through the electrical connections, q_L where:

$$q_E = q_e + q_r + q_L \tag{2.4}$$

Realizing the average kinetic energy of electrons is 2kT, the heat removed by electron emission can be described as:

$$q_e = J_T\left(\phi_E + 2kT_E\right) \tag{2.5}$$

where J_T: The total thermionic emission current described by Equation 2.3; ϕ_E: The cathode work function; k: The Boltzmann constant; and T_E: The temperature of the cathode. The heat removed by thermal radiation can be described in terms of the Stefan-Boltzmann Law as:

$$q_r = \sigma\epsilon(T_E^4 - T_C^4) \tag{2.6}$$

where σ: The Stefan-Boltzman constant (5.67E-12 W/cm^{2}K^4) which is independent of material; ε: Net thermal emissivity of the electrode system ~0.1-0.2; T_E: Temperature of the cathode; and T_C: Temperature of the anode[13]. Because we are analyzing an ideal thermionic converter, the heat conducted through the electrical connection can be neglected resulting in a total equation for the energy conversion efficiency, **η**, of an ideal thermionic converter as[16]:

$$\eta = \frac{J_T V}{q_e + q_r} \tag{2.7}$$

CHAPTER III

EXPERIMENTAL

In this chapter, the details of the diamond emitter growth process and the testing procedure are discussed. A comprehensive description of the testing apparatus is also explained including component selection.

3.1 Device Fabrication

For this study, the thermionic emission of boron-doped microcrystalline diamond films was explored. The testing apparatus designed for this experiment involves directly heating the diamond film's substrate which allows for precise temperature measurements of the diamond emitter. This method requires several considerations for substrate material and geometry that are conducive to accurate measurements. An ideal substrate must have a known emissivity that can be measured with a non-contact dual color pyrometer. The substrate must also have a geometry that allows for it to be heated to temperatures in excess of 1000^{o}C (the minimum limit of the pyrometer) without excessive power requirements. Materials with a large cross-sectional area and small length require more power to heat over thin (small cross-sectional area) longer films. While a "thinner" film will require less power to heat, it will prove extremely brittle after the deposition process and difficult to test so a balance must be struck between power required to heat the device and structural integrity. Finally, a substrate must easily allow diamond nucleation in order for a uniform film to be deposited across its surface. Taking all of these factors into

consideration, 127 µm thick molybdenum foil cut into strips ~4mm wide and ~30mm long were chosen.

The molybdenum foil was prepared for deposition by mild abrasion of the surface which serves two main purposes. First, it removes the native oxide and surface contaminants from the surface providing a clean sample for deposition. Second, it creates localized irregularities that promote diamond nucleation which improves diamond adherence and increases the contact area between the diamond and the molybdenum. The abraded samples are then mechanically nucleated with a nanodiamond paste to provide initial nucleation sites from which the MPCVD diamond to synthesize. These steps were followed by a thorough rinse in methanol to remove any excess diamond residue.

The diamond deposition process was performed with an ASTEX 5kW MPCVD machine. Previous research by our lab has shown that this deposition process can produce boron-doped diamond films with extremely low graphitic content[17]. The deposition process was performed with a microwave power of 3,000 watts, at a pressure of 120 Torr, and a nominal temperature of 800^{o}C for 20 hours. The source gases used for the MPCVD diamond growth process were hydrogen, methane, and trimethylboron (TMB), at 92.5% H_2, 3.5% CH_4, and 4% TMB. The film's grain sizes were observed be on the order of several microns.

3.2 Thermionic emission testing apparatus

Thermionic emission characterization was performed in a high vacuum testing apparatus specifically built to suit the needs of this project. From prior research experience, it was determined that the chamber must be capable of achieving base pressures (pressure before

heating) on the order of $1x10^{-8}$ Torr. These extremely low pressures are required because the molybdenum substrates tend to oxidize at higher pressures when heated to temperatures above 1000^{o}C resulting in unreliable and irreproducible data. Further apparatus considerations from previous research indicated the need for a collector anode completely electrically isolated from the thermionic emitter (the cathode). Past attempts to measure thermionic emission current with an anode placed directly on top of the cathode separated by a dielectric spacer were unsuccessful due high levels of leakage current through the spacers at elevated temperatures.

To address the pressure requirements, a vacuum chamber was fashioned out of a 6 inch 4-way cross. The total volume of this chamber proved small enough to quickly evacuate the chamber yet large enough not to be heated by the cathode which reached temperatures exceeding 1000^{o}C. Heating of the chamber could potentially cause outgassing thereby increasing the chamber pressure during testing. The primary pumping mechanism of this chamber consisted of an ion pump purchased through DUNIWAY STOCKROOM CORP. The pump was attached to the chamber via an "L" shaped nipple which provided no direct line of site from the pump to the collector anode in order to prevent electron emission current arising from the pump from reaching the collector anode. Pressure was constantly monitored with a MKS cold cathode vacuum gauge which was connected to the chamber in the same manner as the ion pump for the same reason.

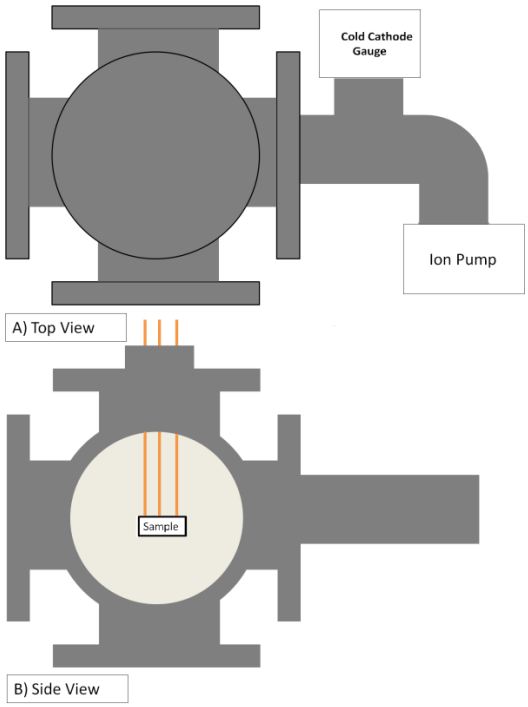

Figure 3.1 A) Top view of the vacuum chamber. Note that there is no direct line of sight between the sample being tested and either the cold cathode gauge or the ion pump. B) Side view of chamber to demonstrate placement of the sample

A sample testing configuration was fashioned from a simple three-pronged high current copper electrical feed through. Two of the prongs were used as both sample holders and points for electrical contact. Brass wire connectors were fitted over these copper prongs to prevent melting when exposed to the high temperatures of the heated sample. Copper alligator clips were utilized to firmly hold the sample in place and to also ensure adequate electrical contact. The third prong was used as an anode which was extremely favorable in consideration of the electrically isolated anode requirement mentioned above.

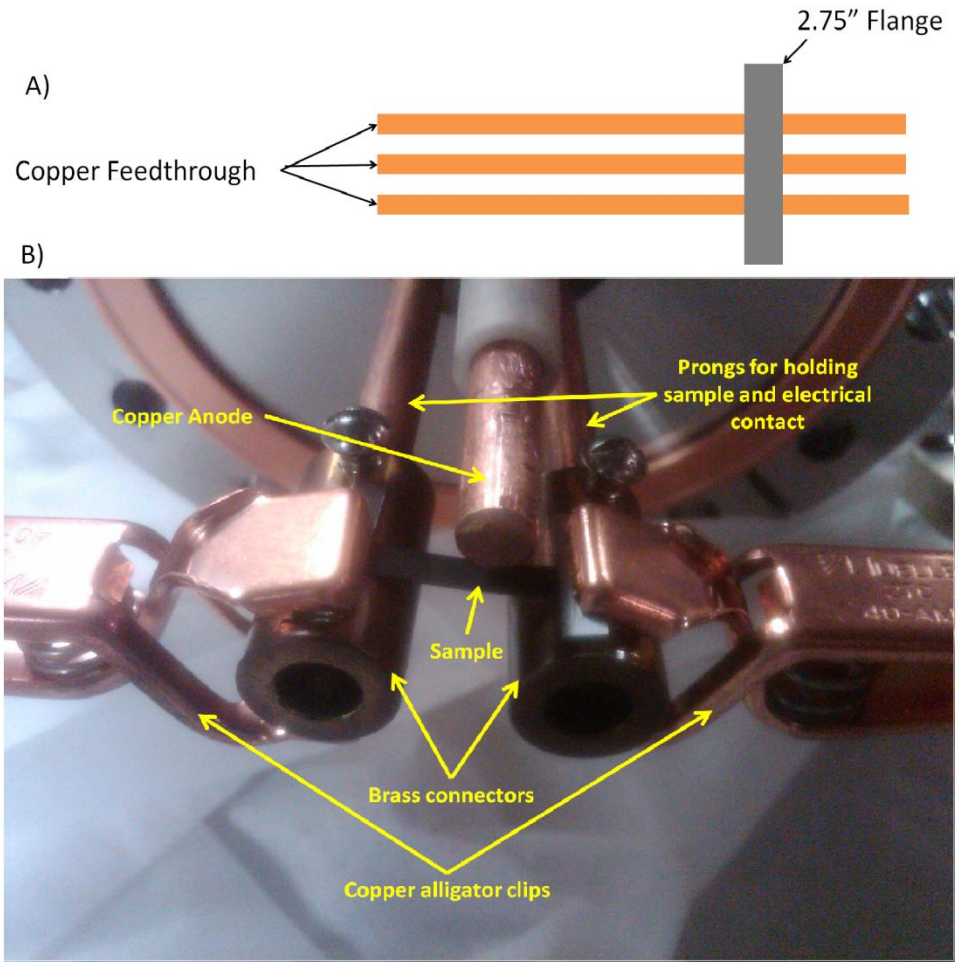

Figure 3.2 A) Diagram of the electrical feedthrough. B) Photograph of the mounted sample

The sample was resistively heated by applying high current (~20 amps) DC power through the two prongs that held the sample. By directly heating the sample, temperature irregularities that would arise from using an external heater due to heat transfer are avoided. DC power was chosen over AC power to reduce noise during the testing. Because this heating method creates not uniformed heating of the sample (i.e. the middle of the sample will be hotter than the ends that are connected to the feedthrough), a quartz aperture was constructed to prevent the collection of electrons from sights that are at different temperatures. The temperature was

constantly monitored with a Raytek Marathon MR optical ratio dual color pyrometer capable of observing temperatures from 1000^{o}C to 3000^{o}C. A dual color pyrometer provides the luxury of being able to measure the temperature of the heated sample outside of the vacuum chamber through a transparent window. A faraday cage was fashioned out of aluminum sheet metal to reduce external electrical interference on device testing.

CHAPTER IV

RESULTS

This chapter presents the results of the diamond deposition including characterization of the films. The thermionic emission current data obtained from the previously discussed methods is reported and the emission current density is analyzed with respect to the Richardson equation in order to extrapolate a work function of boron-doped microcrystalline diamond. Comparison of the results obtained in this research to results obtained from other methods is also discussed.

4.1 Characterization of Diamond Films

A scanning electron micrograph of the diamond films can be observed in Figure 4.1. The average grain size of these films is estimated to be on the order of several microns based on the SEM image at 250X magnification.

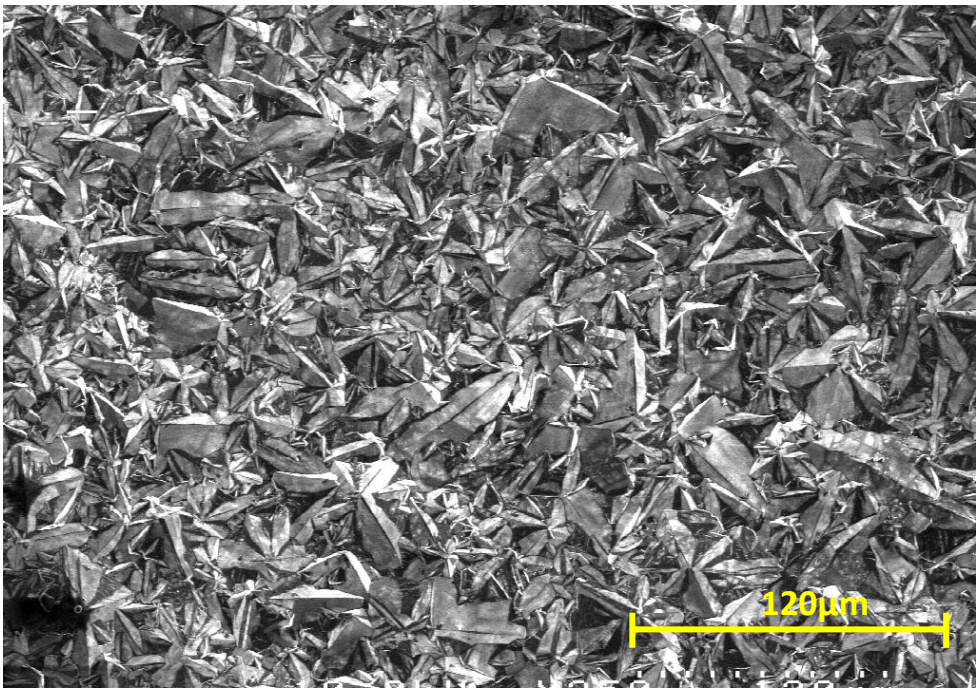

Figure 4.1 Scanning Electron Micrograph of the boron-doped polycrystalline films at 250x magnification and a beam voltage of 10kV

X-Ray Diffraction (XRD) was utilized to characterize the composition of the diamond films [18]. XRD can measure the crystal structure of materials by the diffraction scattering of an incident X-ray beam. By analyzing the diffraction angles, the spacing between adjacent crystal planes can be determined and compared to values for known materials[19].

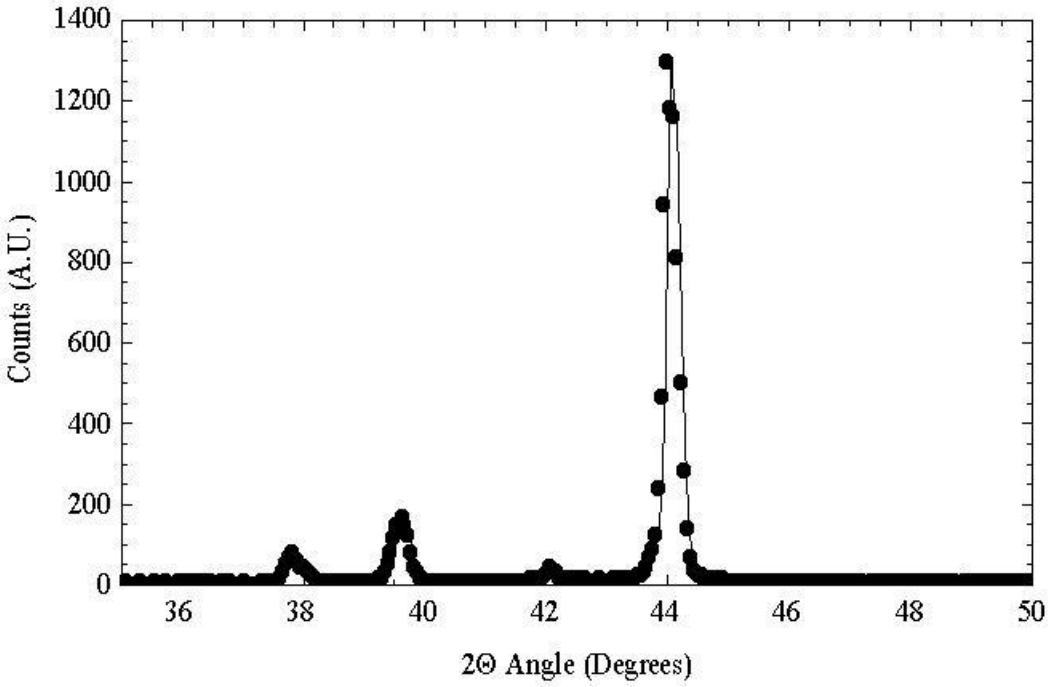

Figure 4.2 X-ray Diffraction measurements on microcrystalline boron doped diamond films. The large peak at 44^{o} points to a predominantly diamond composition. Other peaks are consistent with molybdenum carbide.

Raman spectroscopy performed at Fisk University was used to supplement the XRD results. This analysis indicates that boron-doped diamond films can be deposited with no graphitic content occuring in the deposition process.

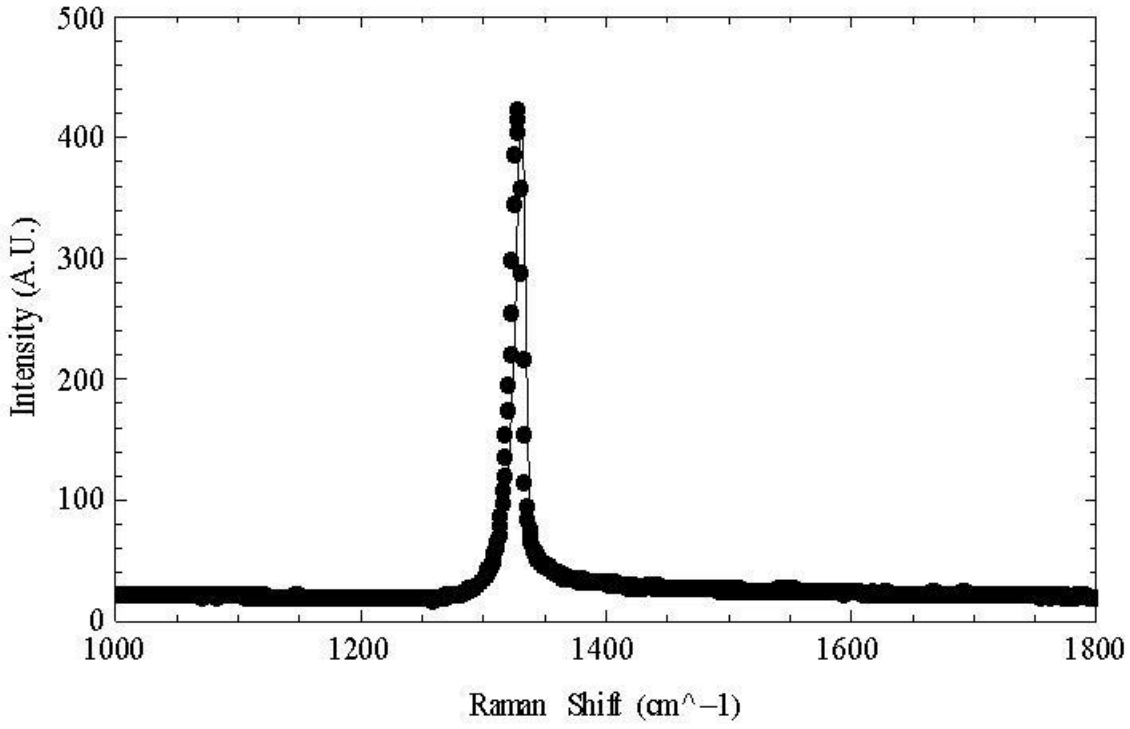

Figure 4.3 Raman Spectrum Analysis of boron-doped polycrystalline diamond sample. The large peak at 1330 with no other distinguishing peaks point to a predominantly diamond sample

4.2 Device Testing

The diamond samples were placed in the testing apparatus, heated, and thermionic emission current was observed through the collector anode biased at 100V which corresponds to an electric field of 0.05V/cm. Examining equation 1.1, it is easily noticed that thermionic emission current does not depend on the applied collector voltage. This small field is necessary to adequately collect all electrons emitted from the sample. A larger collector field would require a modification of the Richardson Equation known as the Schottky effect (Eq. 4.1) to fully describe the emission current. The Schottky effect describes the influence of electric field which lowers the effective barrier for electrons to be emitted and can be described by the Schottky Equation[5].

$$J = AT^2 e^{-(\phi - \Delta\phi)/kT} \tag{4.1}$$

where: $\Delta\phi = \sqrt{\frac{e^3 F}{4\pi\epsilon_o}}$

is the correction factor due to the Schottky effect; e: the electron charge; ϵ_o: is the permittivity of free space; and F: the applied electric field.

By analyzing the emission data from a bare molybdenum film that has a known work function, an electric field of 0.05 V/cm was deemed adequate to collect enough electrons for determining work function but low enough that the Schottky effect is negligible.

With the collector anode fixed at 100 volts, the temperature of the emitter is increased in approximately five degree increments by increasing the power through the sample. The high current power supply necessary to heat the cathode requires the emission current to be observed between the anode voltage power supply and ground which places constraints on the methods capable of measuring this current. Typical picoammeters require that they be placed between the device under test and ground. Because this is not possible, the emission current at each temperature value was measured by taking the voltage drop across a high precision 5MΩ resistor and recorded.

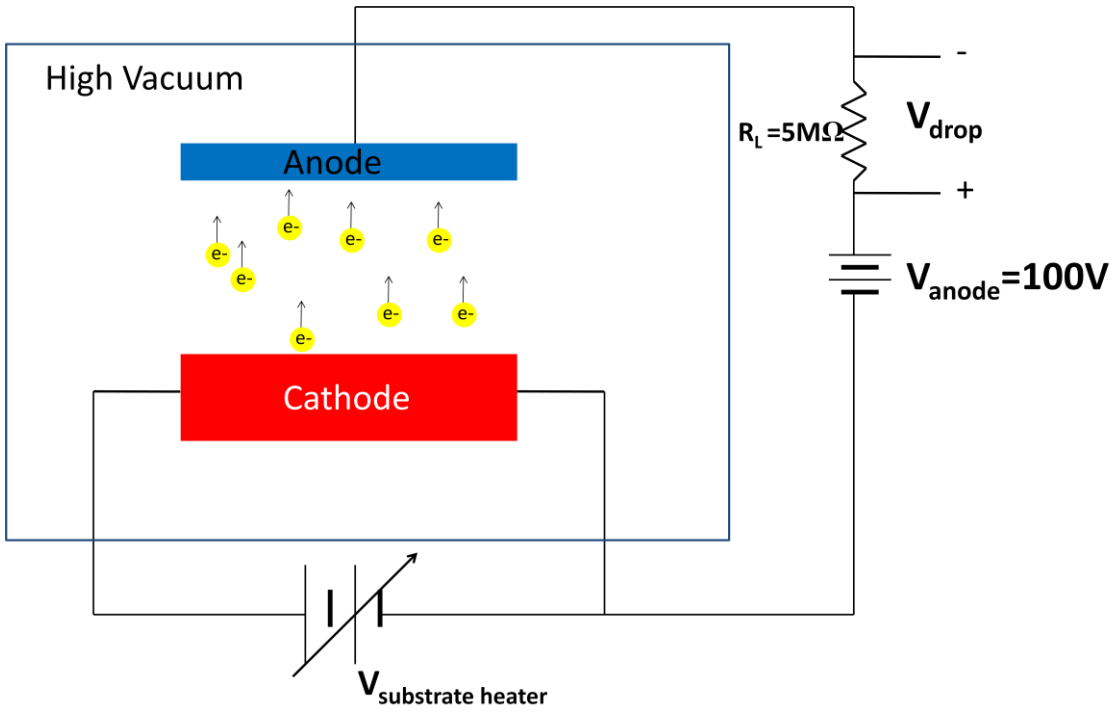

Figure 4.4 Schematic diagram of the thermionic emission testing apparatus including the heater power supply, anode power supply and the voltage drop resistor for measuring the emission current

4.3 Testing results

The emission current fits well with the Richardson Equation (Equation 2.1) as seen in the exponential current increase with temperature in Figure 4.5 implying thermionic emission is the primary mechanism for the observed emission current. It must be noted that during the initial heating of the sample up to the minimum readable value of 1000^{o}C, the emission current decreased dramatically at approximately 800^{o}C and did not stabilize until 1035^{o}C. This observation can only be qualitatively described at this time due to limitations of the pyrometer. This phenomenon has previously been observed by other researchers on nitrogen-incorporated diamond samples[20].

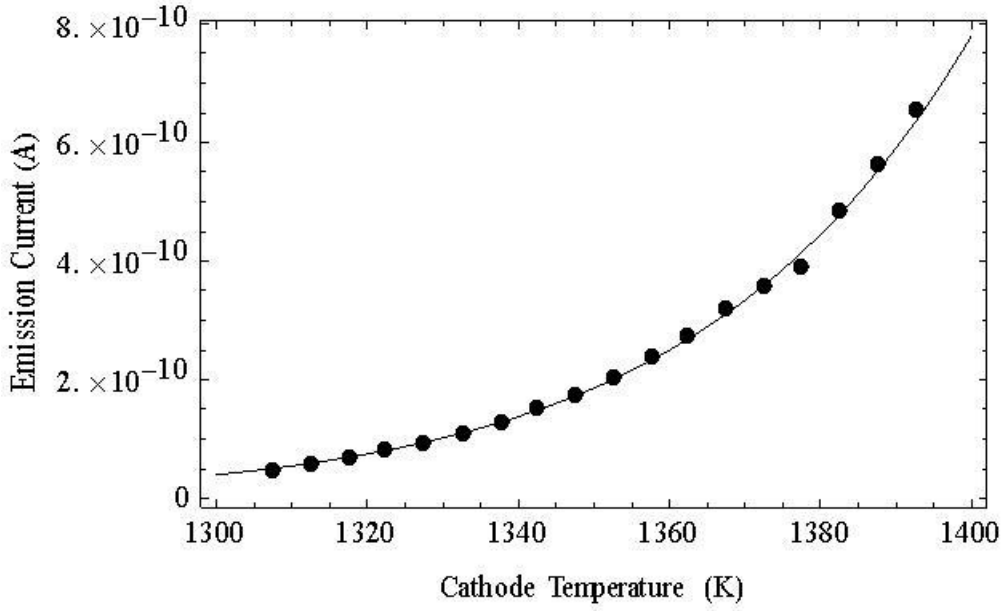

Figure 4.5 Plot of thermionic emission current vs. cathode temperature (points) follows closely with the Richardson equation (solid line).

By rearranging the Richardson Equation and taking the natural logarithm of both sides, an equation for determining the work function of a thermionic emitter from the emission current vs. the cathode temperature data is demonstrated in Equation 4.2.

$$Ln\left(J/_{T^2}\right) = -\Phi/_{kT} + Ln(A) \tag{4.2}$$

where: J, A, T, k, A, and ϕ are the same values as defined in Equation 2.1.

By plotting the left side of this equation against -1/kT, the resulting plot has a slope equal to the work function of the material and a y-intercept equal to Ln(A). The plot of Equation 4.2 (Figure 4.6) displays a linear fit with an r^2= 0.999. The slope of 4.43 corresponds to the work function of the boron-doped sample over this temperature range with a Richardson Constant of ~60A/cm^2.

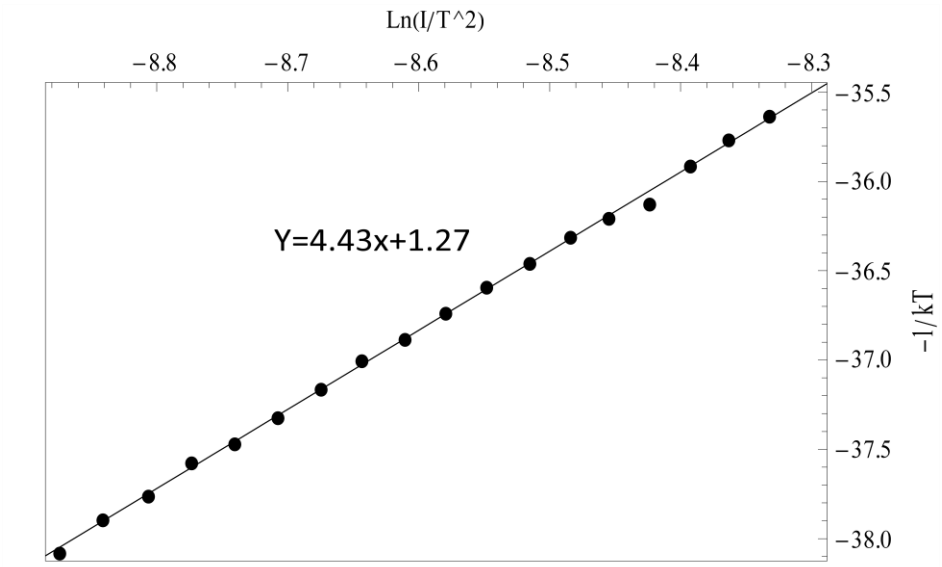

Figure 4.6 Plot of Eq. 4.2 where the slope of 4.43ev is the materials work function and the y-intercept of 1.27 is the natural log of the Richardson Constant

The correlation coefficient (r^2) value of 0.999 is extremely close to the optimal value of 1 demonstrating a strong goodness of fit of the observed data to the theoretical model derived from the Richardson Equation.

4.4 Comparison to previously reported work

Numerous previous studies on similar diamond samples have been undertaken which agree strongly with the values reported in this research. The work by V. S. Robinson et al. examined the work function of boron-doped polycrystalline diamond samples at elevated temperatures by use of an electron energy analyzer[21]. In the study, diamond films were heated by a molybdenum button heater with the temperature monitored by a k-type thermocouple in a

high vacuum environment. The energy of the thermally emitted electrons was measured with a hemispherical energy analyzed at known temperatures. The study determined the work function of the diamond samples to be 4.52eV at a temperature of 1085^{o}C which is within the temperature range tested in this research. The paper also observed the work function change from 3.95eV at 750^{o}C to the 4.52eV value mentioned above. This observation agrees with the emission current decrease discussed in Section 3.1. The 0.09eV discrepancy between work function values most likely occurs because our measurements were taken over a range of temperatures where as the other method extracted a value at a specific temperature.

The work of M. Suzuki et al. examined the low temperature thermionic emission from nitrogen incorporated diamond films[22]. Though the samples tested were different, the material, diamond, was the same and because the Richardson constant is material specific, not doping specific, the Richardson constants should be similar. The diamond films were radiatively heated and the temperature was monitored with a noncontact pyrometer. The emission current was observed from a collector anode in a similar manner to methods discussed in this research. The Richardson constant was calculated to be 70A/cm^2 which agrees closely with the 60A/cm^2 value observed in this paper.

CHAPTER V

SUMMARY

In this research, boron-doped polycrystalline diamond films were synthesized and the thermal electron emission properties were examined for their use in thermionic energy conversion. A method for characterizing these films was devised which provides accurate results with minimal complexity. This chapter highlights the important findings of this research and attempts to provide the potential output power characteristics of a thermionic converter with boron-doped diamond as a cathode. Finally, recommendations for future work are discussed.

5.1 Characterization of thermionic emission

A testing apparatus has been created for testing and characterizing the thermal electron emission properties of diamond films with respect to energy conversion. In this testing apparatus, diamond films were deposited on molybdenum substrates, resistively heated to temperatures exceeding 1000^{o}C in a high vacuum environment, and the thermionic emission current was observed. This method has produced accurate results that not only follow closely with the equations governing thermionic emission but also agree with previously reported values on similar films which use much more sophisticated methods for calculating working function[21, 22].

The close agreements of the emission current values with the Richardson equation demonstrate boron-doped diamond as an extremely reliable electron emitter with potential uses

outside of energy conversion. Precision electron emitters are highly desired in numerous applications such as electron microscopy where known emission current values are necessary for high resolution imaging.

5.2 Potential output power characteristics

Though the thermal emission parameters derived from boron-deoped polycrystalline diamond in this experiment are not idea for an efficient thermionic converter, the potential power conversion capabilities must be discussed. An estimation of the potential output power characteristics can be undertaken by selecting an anode with an extremely low work function. Nitrogen incorporated nanodiamond has demonstrated a work function of 1.29eV[23] which allows for a large built-in potential of 3.14V (as described in section 2.3). Examining the total emission current and accounting for reverse emission current from the cathode as discussed in Equation 2.3, the total emission current can be plotted with respect to cathode temperatures at various anode temperatures.

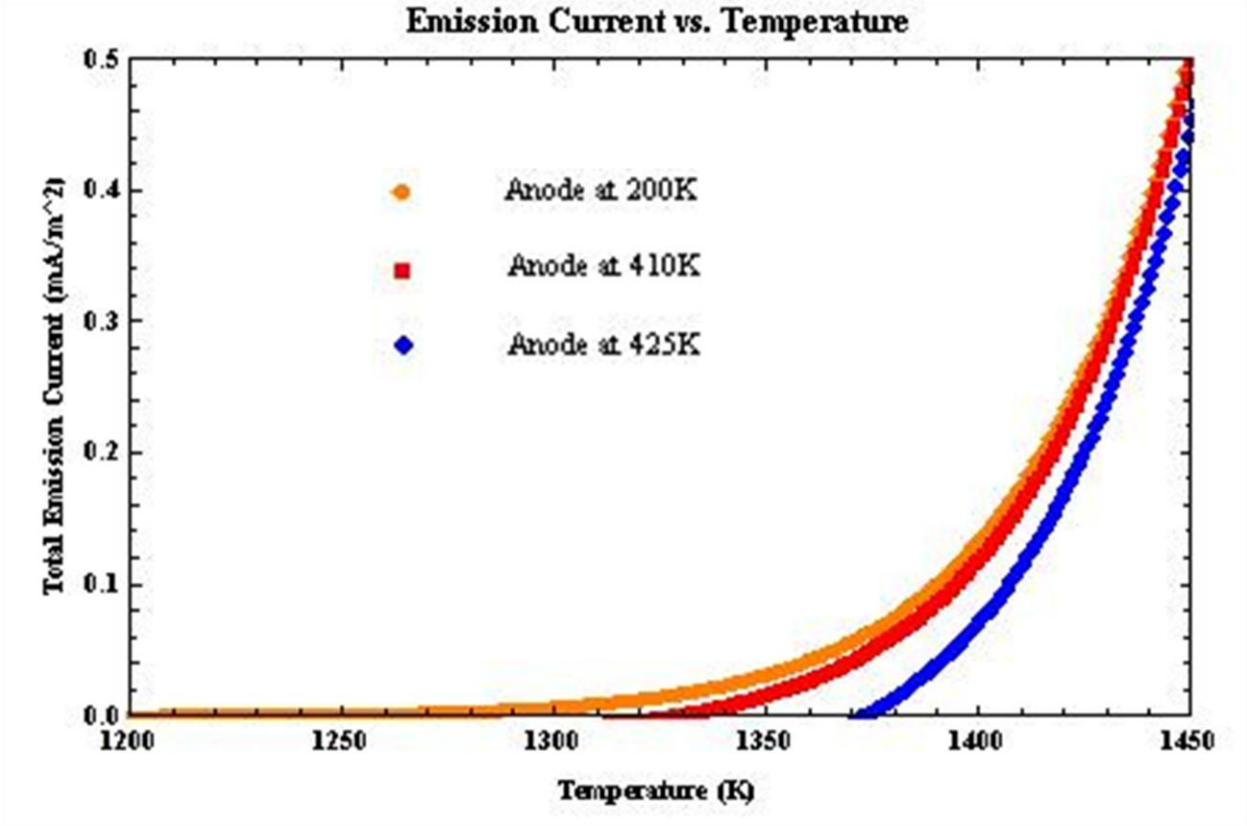

Figure 5.1 Theoretical output current values from thermionic emitter with a boron-doped diamond cathode and a low work function nitrogen incorporated anode

The total output power density of this theoretical device can be calculated by multiplying the built-in potential by the output emission current density. It must be noted that these output values represent an ideal thermionic converter where emission current is not space charge limited and the voltage drop resulting from electrical connections is neglected. It can be seen from Figure 5.2 that this device could achieve power output densities of around 1.5mA/m^2.

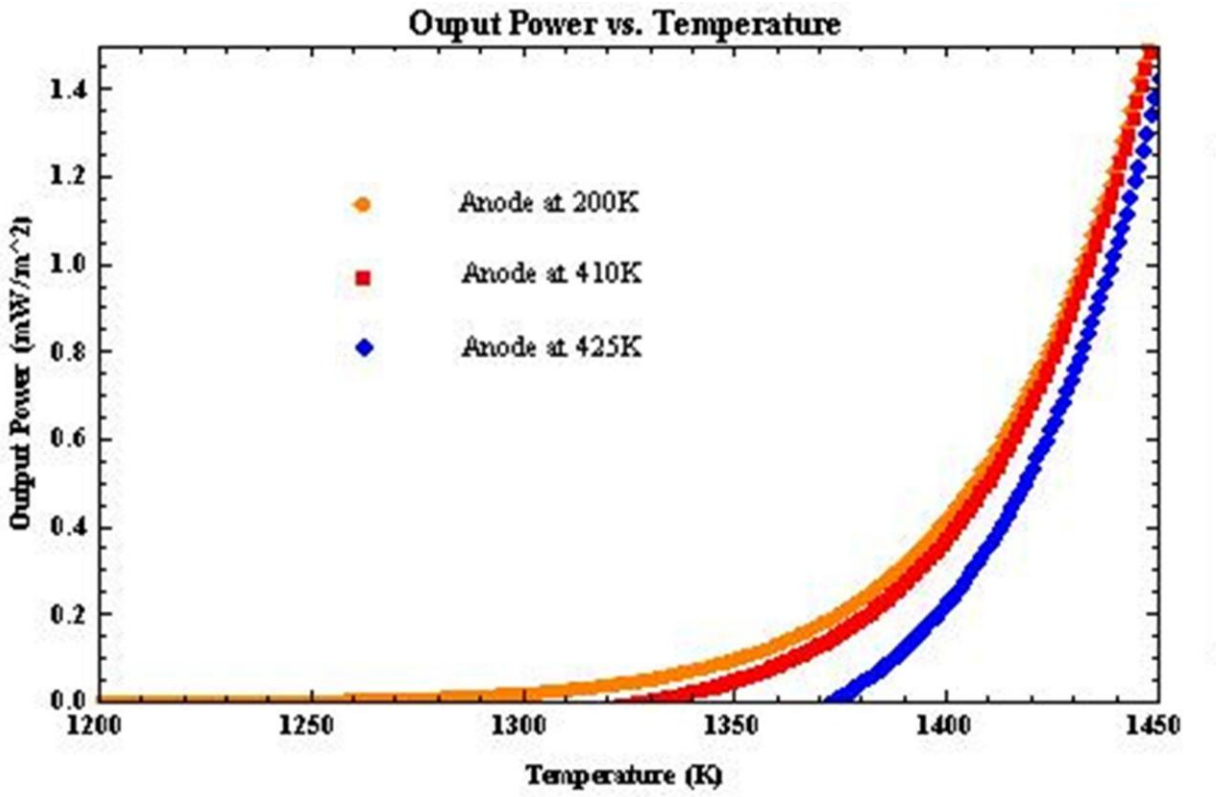

Figure 5.2 Output power performance of an ideal thermionic converter with a boron-doped diamond cathode and a low work function nitrogen incorporated diamond anode. Space charge effects and voltage drops from electrical connections have been neglected.

5.3 Recommendations

The primary objective of this research project is the characterization of diamond films for use in thermal energy conversion via thermionic emission. The high emission current densities of boron-doped polycrystalline diamond films demonstrate that this is a real possibility. As discussed earlier, the two material properties that relate to an efficient energy converter are the material's work function and Richardson constant. The work function value of 4.43eV of boron-doped diamond derived in this project requires extremely high temperatures in order to produce an efficient emitter. This could possibly be improved by utilizing diamond films with an n-type

dopant rather than boron which is a p-type dopant. From the band diagram in Figure 1.2, it can be seen that an n-type dopant would move the Fermi level closer to the conduction band thereby decreasing the material's work function.

During the testing of these films, a significant current decrease was observed at temperatures around 800^{o}C. This should be further investigated because boron-doped diamond could have different emission characteristics at these lower temperatures. Testing at lower temperatures will require a new pyrometer capable of measuring temperatures below 800^{o}C (preferably able to observe temperatures from 600^{o}C and higher). This new pyrometer will also allow other films to be characterized at lower temperatures. By finding materials which operate with useable current densities at lower temperatures, a more practical thermal energy converter can be envisioned.

Finally, a stand-alone thermionic power converter should be constructed. This should consist of an electrically isolated cathode and anode where the cathode is heated by a method other than resistive heating. Resistive heating of the cathode provides an adequate method for heating and characterizing the thermal emission properties of various films but it is not favorable to a thermionic converter due to the power that is put into the system. For a thermionic power converter, a non-contact heat source such as a flame or radiative heating would be most favorable.

REFERENCES

[1] S. J. Pearton, "Wide Bandgap Semiconductors - Growth, Processing and Applications," William Andrew Publishing/Noyes, 2000, p. 507.

[2] J. H. Ingold, "Calculation of the Maximum Efficiency of the Thermionic Converter," *Journal of Applied Physics,* vol. 32, pp. 769-772, 1961.

[3] R. J. Zhang, *et al.*, "Characterization of heavily boron-doped diamond films," *Diamond and Related Materials,* vol. 5, pp. 1288-1294, 1996.

[4] F. J. Himpsel, *et al.*, "Quantum photoyield of diamond(111)& A stable negative-affinity emitter," *Physical Review B,* vol. 20, p. 624, 1979.

[5] E. L. Murphy and R. H. Good, "Thermionic Emission, Field Emission, and the Transition Region," *Physical Review,* vol. 102, p. 1464, 1956.

[6] J. L. Davidson, *et al.*, "Vacuum Cold Cathode Emitter Electronic Devices Comprised of Diamond or other Carbons," in *University/Government/Industry Micro/Nano Symposium, 2008. UGIM 2008. 17th Biennial,* 2008, pp. 102-106.

[7] W. P. Kang, *et al.*, "Physical characterization of diamond pyramidal microtip emitters," 1997, pp. 460-463.

[8] W. P. Kang, *et al.*, "Characterization of the Microstructure of Diamond Pyramidal Microtip Emitters," presented at the International Conference on the New Diamond Science and Technology, Tours, France, 1996.

[9] W. P. Kang, *et al.*, "Diamond vacuum field emission devices," *Diamond and Related Materials,* vol. 13, pp. 1944-1948, Nov-Dec 2004.

[10] "International Energy Outlook 2010 - Highlights," U. S. E. I. Administration, Ed., 2010, p. 2.

[11] C. Bauer, *et al.*, "Radiation hardness studies of CVD diamond detectors," *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment,* vol. 367, pp. 207-211, 1995.

[12] O. W. Richardson, "The Electrical Conductivity Imparted to a Vacuum by Hot Conductors," *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character,* vol. 201, pp. 497-549, 1903.

[13] *Fundamentals Handbook of Electrical and Computer Engineering* vol. II: John Wiley & Sons, Inc., 1983.

[14] F. A. M. Koeck and R. J. Nemanich, "Emission characterization from nitrogen-doped diamond with respect to energy conversion," *Diamond and Related Materials,* vol. 15, pp. 217-220.

[15] F. A. M. Koeck, *et al.*, "Thermionic electron emission from low work-function phosphorus doped diamond films," *Diamond and Related Materials,* vol. 18, pp. 789-791.

[16] A. Schock, "Optimization of Emission-Limited Thermionic Generators," *Journal of Applied Physics,* vol. 32, pp. 1564-1570, 1961.

[17] A. Wisitsora-at, *et al.*, "Efficient electron emitter utilizing boron-doped diamond tips with sp2 content," *Applied Surface Science,* vol. 146, pp. 280-286, 1999.

[18] K. Fabisiak and F. Rozpłoch, "ESR and X-ray diffraction studies of the CVD diamond films," *Applied Magnetic Resonance,* vol. 12, pp. 53-59, 1997.

[19] J. F. Shackelford, *Materials Science for Engineers*. Upper Saddle River, New Jersey: Pearson Prentice Hall, 2005.

[20] M. Kataoka, *et al.*, "Thermionic electron emission from nitrogen-doped homoepitaxial diamond," *Diamond and Related Materials,* vol. 19, pp. 110-113.

[21] V. S. Robinson, *et al.*, "Thermionic emission from surface-terminated nanocrystalline diamond," *Diamond and Related Materials,* vol. 15, pp. 1601-1608, 2006.

[22] M. Suzuki, *et al.*, "Low-temperature thermionic emission from nitrogen-doped nanocrystalline diamond films on n-type Si grown by MPCVD," *Diamond and Related Materials,* vol. 18, pp. 1274-1277, 2009.

[23] F. A. M. Koeck and R. J. Nemanich, "Low temperature onset for thermionic emitters based on nitrogen incorporated UNCD films," *Diamond and Related Materials,* vol. 18, pp. 232-234.